

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
30 August 2001 (30.08.2001)

PCT

(10) International Publication Number
WO 01/62221 A1

(51) International Patent Classification⁷: **A61K 7/13**

(21) International Application Number: **PCT/US01/05598**

(22) International Filing Date: 22 February 2001 (22.02.2001)

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
0004413.1 24 February 2000 (24.02.2000) **GB**

(71) Applicant (for all designated States except US): **THE PROCTER & GAMBLE COMPANY [US/US]**; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **PRATT, Dominic** [GB/GB]; 11a Chobham Road, Sunningdale, Berkshire SL5 0DU (GB). **DIAS, Louis, Carlos** [US/GB]; 26 Highgate House Abbots Drive, Virginia Water, Surrey GU25 4SE (GB). **UNDERWOOD, Matthew** [GB/GB]; 453 Victoria Road, South Ruislip, Middlesex HA4 0EQ (GB). **JAMES, Delyth, Angharad** [GB/GB]; 27 Fishguard Road, Letterston, Haverfordwest, Pembrokeshire, South Wales SA62 5UG (GB).

(74) Common Representative: **THE PROCTER & GAMBLE COMPANY**; c/o Timothy B. Guffey, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AT (utility model), AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, CZ (utility model), DE, DE (utility model), DK, DK (utility model), DM, DZ, EE, EE (utility model), ES, FI, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 01/62221 A1

(54) Title: **PRETREATMENT FOR HAIR COLORING COMPOSITIONS AND METHODS**

(57) Abstract: The present invention provides a method of altering hair color comprising the steps of (a) applying a pretreatment composition, which has a pH in the range 1 to 13, to the hair to be colored, the pretreatment composition being substantially free of hair color altering agents; and (b) applying to the hair, in a subsequent step, a color altering composition which has a pH in the range 1 to 13, and the pH of the pretreatment composition is higher than the pH of the color altering composition; wherein the pretreatment composition is not rinsed from the hair prior to the application of the color altering composition.

Pretreatment for Hair Coloring Compositions and MethodsTechnical Field

This invention relates to hair coloring compositions and methods, more particularly to decreasing the extent of damage to hair during the application of hair color altering compositions by pretreating hair prior to
5 altering the color of the hair.

Background of the Invention

The problems associated with coloring hair are numerous, including the delivery of precise colors to the hair, increasing the retention time of
10 color in the hair, damage imparted to the hair during the coloring process, inconsistent coloration of the hair due to irregular uptake of hair coloring agents along the length of the hair shaft and adverse effects on the hair and skin of the user, such as brittle hair, irritation of the skin, staining and lachrymatory effects.

15 It would be highly desirable to develop a system for increasing color uptake and color retention on the hair whilst decreasing damage to the hair and reducing other adverse effects to the user.

Various approaches to hair dyeing have been developed, including direct action dyes, natural dyes, metallic dyes and oxidative dyes.
20 To color hair using oxidative dye technology the hair is generally treated with a mixture of oxidative hair coloring agents and an oxidising agent. Hydrogen peroxide is the most commonly used oxidising agent. However, in addition to oxidising the oxidative coloring agents, hydrogen peroxide treatment of the hair can also solubilise and decolorise the colored melanin component in
25 the hair. This can lead to hair damage, resulting in, for example, brittleness. This is in part due to the conditions of conventional oxidative treatment, as part of the hair coloring process. Normally coloring is conducted at high color altering composition pH ($> \text{pH } 9$). It also exposes the hair to the color altering composition for an extended period (usually from 10 to 60 minutes) and exposes the hair to a relatively high concentration of oxidising solution
30 (between about 20% to about 40% volume of oxygen i.e. about 6 - 12% wt.).

These conditions are usually considered necessary in order to deliver effective dye oxidation.

Oxidative hair coloring agents and peroxygen oxidising agents can be used to deliver a variety of hair colors to the hair. However substantial improvement is desirable in the areas of improved color saturation, improved color development, precise initial color consistency, improved wash fastness, improved hair condition and lower levels of hair damage.

Typically, hair coloring compositions containing oxidative hair coloring agents are formulated at high pH (from about pH 9 to about pH 12) and commonly contain, in addition to the oxidative hair coloring agents and an inorganic peroxygen oxidising agent, peroxide activating agents and a variety of additional cosmetic agents. The hair coloring compositions also commonly contain coloring agent and peroxygen oxidising agent stabilising agents.

We disclose in our publication application WO98/27945 that the combination of inorganic peroxygen oxidising agents with one or more oxidative hair coloring agents in a composition having a pH below the internal pH of hair, between about pH 1 and about pH 6, optionally comprising certain additional oxidising agents. It was disclosed that the efficiency of color development (color change) from the inorganic peroxygen oxidising agents and particular oxidative hair coloring agents is improved under the low pH conditions (about 1 to 6). In particular, it was disclosed that these low pH hair coloring compositions can deliver good hair coloring attributes with reduced hair damage. However, there is room for improvement, in particular in terms of color uptake. Although these systems are known, in practice the vast majority of oxidative hair coloring products presently on the market retain the high pH conditions, and associated disadvantages, discussed above.

It is known that enhanced oxidative hair coloring agent oxidation can be achieved via the use of a hair swelling agent (HSA).

HSAs enhance the coloring process by swelling the hair fibres to aid the diffusion of the peroxygen oxidising agent and the oxidative hair coloring

agents into the hair. This enables faster, more thorough dye oxidisation and hair coloring.

The most commonly used HSA is an aqueous (alkaline) solution containing a source of ammonia, such as ammonium hydroxide. However, ammonia can cause skin irritation and in addition has an undesirable odour and can cause lachrymatory effects.

It is disclosed in our copending application GB 9924885.8 that a HSA may be incorporated into a high pH oxidative coloring composition above. These hair coloring compositions have the disadvantage of having a high pH, thus tend to cause greater levels of damage to the hair than a low pH, coloring system.

It would be desirable to provide hair coloring methods which deliver a combination of improved hair coloring attributes, such as longer lasting color (reduced fade), initial color generation, increased color uptake and color consistency across hair types (ie. Such as hair of varying age and condition i.e. virgin (untreated), grey, permed, bleached etc).

It would also be desirable to provide hair coloring methods which provide a combination of lower levels of skin irritation and/or skin staining versus conventional systems, reduced damage to the hair fibres and reduced staining of skin and an acceptable odor.

It would further be desirable to provide hair coloring methods which exhibit increased efficacy (improved color development). Color development means the change in the hair color, expressed in terms of Delta E (ΔE).

US 5,100,436 discloses aqueous solutions of transition metal ions used to catalyze the oxidative dyeing of virgin hair. Specifically the process involves using transition metal ions complexed with dipyridyl or o-phenanthroline chelating agents as an aqueous pretreatment for hair. Subsequently to the application of the pretreatment composition an oxidative dyeing mixture is applied to the hair. The pretreatment is rinsed off the hair prior to the application of the oxidative dyeing mixture.

GB 1,469,265 discloses a process for coloring hair, comprising treating the hair with an acid dye in aqueous solution subsequent to the application of

a water-soluble composition comprising a cationic polymer selected from water-soluble acid salts. The pH range for the compositions of this invention are from 2.5 to 7.0. The presence of a pH differential between the first and second treatment compositions is not disclosed.

5 US 4,425,132 describes a two-stage process for dyeing keratin fibres, which involves treating the fibres with a first composition at a first pH and subsequently, without rinsing, treating the fibres with a second composition at a second pH, at least one of the compositions containing a dyestuff for the fibres, and the second pH being different from the first pH so as to modify the
10 effect of at least one active ingredient on the fibres. In practice the first applied composition appears to contain a dyestuff, the problem being to apply two different coloring agents which work most effectively at different pH levels.

J. Kelson, *et al*, (Proc. Int. Wool Res. Conf., 8th, Volume 1, 459-68) describe the use of dye diffusion techniques to study the histological changes
15 in Negroid hair treated with sodium hydroxide. The disclosure is not concerned with altering the color of the hair but is instead concerned with using dye techniques as a research tool to study other phenomena.

JP 4069324 discloses the use of non-oxidative hair coloring agents having a pH of 2.5 to 7.5 in conjunction with pretreatment compositions.

20 Thus none of these disclosures is concerned with the problem addressed by the present invention which is the provision of methods for coloring hair using the effective oxidative coloring systems but reducing hair damage and other undesirable effects, at the same time as maintaining or even improving color uptake and/or retention.

25 EP-B-435,012 describes the use of HCO_3^- generating compounds in hair dyeing compositions. This is used in combination with an alkali, hydrogen peroxide and coloring agents. The pH of the final treatment composition applied to the hair is in the range 6.5 - 7.9. The components which form this composition are provided separately and premixed prior to
30 simultaneous application of all the components to the hair. Although concerned with damage limitation to the hair there is room for improvement in both damage limitation and color uptake by the hair and color generation.

Summary of the Invention

The present invention provides, in a first aspect, a method of altering hair color comprising the steps of:

- 5 (a) applying a pretreatment composition, which has a pH in the range 1 to 13, to the hair to be colored, the pretreatment composition being substantially free of hair color altering agents; and
- (b) applying to the hair, in a subsequent step, a color altering composition which has a pH in the range 1 to 13, and the pH of the pretreatment composition is higher than the pH of the color altering composition; wherein the pretreatment composition is not
10 rinsed from the hair prior to the application of the color altering composition.

Generally the time for which the pretreatment step is in contact with the hair before application of the color altering composition is significantly shorter
15 than the time for which the color altering composition is in contact with the hair.

We have found that various potentially damaging components commonly included in hair color altering treatments do not require the same amount of time on the hair as other compositional components in order to be effective. It is essential that, for instance, the oxidising agent and oxidative coloring agents
20 remain on the hair for an extended amount of time. Other potentially damaging components (eg., ammonia) require a shorter contact time.

The method of the present invention enables the amount of time such damaging components spend on the hair to be lowered compared to hair color altering methods that do not include a pretreatment, by including these in the
25 pretreatment composition.

Pretreatment has surprisingly also been found to increase the efficacy of oxidising agent/oxidative coloring agent based systems.

The use of the method of the invention also surprisingly results in a reduced propensity for the coloring components to be lost from the hair due to
30 washing. This process is known as wash fade and can be measured over a period of time, usually in terms of number of washes of the colored hair. Fluorescence studies have shown that the application of a coloring composition

without a pretreatment composition leads to a certain degree of fade. In pretreated hair, in contrast, we have observed that color is less easily removed from the hair, resulting in less fade.

Damage to hair is measured in terms of concentration levels of cysteic acid in the hair. The damaging components in the color altering composition, for example the oxidising agent, can cause scission of cysteine bonds in the hair. This can cause production of cysteic acid, the levels of which can be measured and correlated to the amount of damage inflicted on the hair. The concentration of cysteic acid is generally measured by spectrophotometric methods, discussed in greater detail below.

The present invention can decrease damage compared to commercial high pH hair coloring methods which do not include a pretreatment step but instead include a simultaneous application of all components.

The present invention provides an increased ability to color the hair compared to a hair color altering treatment having a pH of 1 to 7 which is applied without a pretreatment but instead includes an application of all components.

The hair to be treated may be 'living', i.e. on a living body or may be 'non-living' i.e. in a wig, hairpiece or other aggregation of non-living fibres, such as those used in textiles and fabrics. Mammalian, especially human hair is preferred. However wool, fur and other melanin containing fibres are suitable substrates for use in the methods used in the present invention.

The pretreatment composition is applied to the hair prior to the color altering composition. In aspects of the invention discussed below, the pretreatment composition may be removed, for example by rinsing, prior to application of the color altering composition, although in preferred embodiments and in the first aspect of the invention the pretreatment composition is not removed before application of the color altering composition.

An essential feature of the present invention is the provision of a two step treatment. The first step involves the pretreatment of the hair with a composition having a pH in the range of 1 to 13, preferably 6 to 13, more

preferably 7.5 to 12, more preferably 8 to 10, most preferably 8.5 to 9.5 and especially 8.7 to 9.2.

A further essential feature of the present invention is that the pretreatment composition has a higher pH than that of the color altering composition. Preferably the difference in pH of the two compositions is greater than 0.5 pH units, preferably greater than 1 pH unit, more preferably greater than 2 or 3 pH units.

A most preferred embodiment of the present invention provides a pretreatment composition having a pH in the range 8.5 to 9.5 and a color altering composition having a pH of no greater than 6, more preferably no greater than 5.5.

The pretreatment composition is not a color altering composition and is substantially free of any oxidative or non-oxidative hair coloring agents and oxidising agents. That is, any oxidative or non-oxidative hair coloring agents, or oxidising agents that are present in the pretreatment composition are present in an amount of less than 2%, preferably less than 1%, more preferably less than 0.5%, most preferably less than 0.1%.

The pretreatment composition generally comprises an alkalising agent. This may be, for instance, an organic or inorganic base selected from sodium hydroxide, ammonia, potassium hydroxide, piperidine, an alkylamine, such as mono-, di- or tri-methylamine, mono-, di- or tri-ethylamine, mono-, di- or tri-propylamine, mono-, di- or tri-butylamine, mono-, di- or tri-isopropylamine, isobutylamine, tert.-butylamine, an amylamine, myristylamine or laurylamine, ethylenediamine, an alkanolamine, such as mono-, di- or tri-ethanolamine, mono-, di- or tri-propanolamine, mono-, di- or tri-isopropanolamine or 2-amino-2-methylpropanol, 2-amino-2-methylpropane-1,3-diol, an alkylalkanolamine; sodium carbonate, potassium carbonate, ammonium carbonate, sodium hydrogen carbonate, potassium hydrogen carbonate, ammonium hydrogen carbonate, sodium carbamate, potassium carbamate, ammonium carbamate, and mixtures thereof.

The alkalising agent has the effect of swelling the hair and aiding in the solubilisation of melanin, which aids in improving color uptake. We find that the

swelling of the hair using the pretreatment composition of the present invention causes little damage to the hair.

Preferably the alkalising agent is a salt which, upon dissolution, produces HCO_3^- ions.

5 In a particularly preferred embodiment the alkalising agent is selected from ammonium carbonate, ammonium carbamate and ammonium hydrogen carbonate, most preferably ammonium carbonate.

Preferably the alkalising agent is included at a concentration (by weight) of from about 0.01% to about 10%, more preferably from about 0.1% to about 10
10 5%, and especially from about 1.5% to about 5.5% based on total pretreatment composition.

In a preferred embodiment, the pretreatment is applied directly to the hair and is left in place for between 30 seconds and 20 minutes, preferably 1-10 minutes, more preferably 2-6 minutes, most preferably 3-5 minutes application
15 of the color altering composition without prior removal of the pretreatment composition.

The pretreatment composition may comprise a number of other components in addition to the ammonium carbonate/ammonium hydrogen carbonate or other alkalising agent, as follows:

20 Solvents/Diluents

The alkalising agent is generally prepared and presented as an aqueous solution, preferably containing from 5 - 99.5% water, more preferably 10 - 96% water.

Additionally or (less preferably) instead of water, the pretreatment
25 composition may comprise an organic solvent, preferably 0.1 - 50% of an organic solvent, more preferably 0.2 - 10%. Preferred organic solvents suitable for use as additional diluents herein include C_1 - C_{20} mono- or polyhydric alcohols and their ethers and glycerine, with monohydric and dihydric alcohols and their ethers preferred. In these compounds, alcoholic residues containing
30 2 to 10 carbon atoms are preferred. Thus, preferred solvents include ethanol, isopropanol, n-propanol, butanol, propylene glycol, ethylene glycol monoethyl ether, and mixtures thereof.

Principal diluent means the solvent in the composition which is present at a higher level than the total level of all other diluents. Water is the preferred principal diluent in the compositions according to the present invention and it is most preferred that water is substantially the only diluent.

5 Surfactant

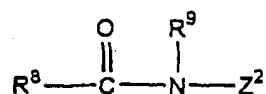
The pretreatment composition may also comprise a surfactant system. Generally 0.05 - 10% of a surfactant is used, more preferably 0.1 - 2%, most preferably 0.2 - 0.5%. Suitable surfactants for inclusion in the compositions of the invention generally have a lipophilic chain length of from about 8 to about
10 22 carbon atoms and can be selected from anionic, cationic, nonionic, amphoteric, zwitterionic surfactants and mixtures thereof.

(i) Anionic Surfactants

Anionic surfactants suitable for inclusion in the pretreatment composition includes alkyl sulphates, ethoxylated alkyl sulphates, alkyl glyceryl ether
15 sulfonates, methyl acyl taurates, fatty acyl glycines, N-acyl glutamates, acyl isethionates, alkyl sulfosuccinates, alkyl ethoxysulphosuccinates, alpha-sulfonated fatty acids, their salts and/or their esters, alkyl ethoxy carboxylates, alkyl phosphate esters, ethoxylated alkyl phosphate esters, alkyl sulphates, acyl sarcosinates and fatty acid/protein condensates, and mixtures thereof.
20 Alkyl and/or acyl chain lengths for these surfactants are C₁₂-C₂₂, preferably C₁₂-C₁₈ more preferably C₁₂-C₁₄.

(ii) Nonionic Surfactants

The pretreatment composition of the invention can also comprise water-soluble nonionic surfactant(s). Surfactants of this class include C₁₂-C₁₄ fatty
25 acid mono- and diethanolamides, sucrose polyester surfactants and polyhydroxy fatty acid amide surfactants having the general formula below.



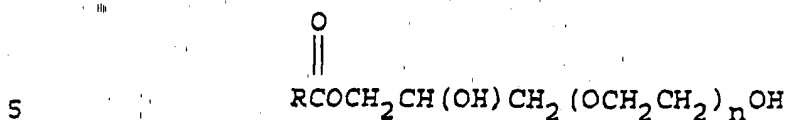
30 The preferred N-alkyl, N-alkoxy or N-aryloxy, polyhydroxy fatty acid amide surfactants according to the above formula are those in which R⁸ is C₅-C₃₁ hydrocarbyl, preferably C₆-C₁₉ hydrocarbyl, including straight-chain and

branched chain alkyl and alkenyl, or mixtures thereof and R^9 is typically hydrogen, C_1 - C_8 alkyl or hydroxyalkyl, preferably methyl, or a group of formula $-R^1-O-R^2$ wherein R^1 is C_2 - C_8 hydrocarbyl including straight-chain, branched-chain and cyclic (including aryl), and is preferably C_2 - C_4 alkylene, R^2 is C_1 - C_8 straight-chain, branched-chain and cyclic hydrocarbyl including aryl and oxyhydrocarbyl, and is preferably C_1 - C_4 alkyl, especially methyl, or phenyl. Z^2 is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 2 (in the case of glyceraldehyde) or at least 3 hydroxyls (in the case of other reducing sugars) directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z^2 preferably will be derived from a reducing sugar in a reductive amination reaction, most preferably Z^2 is a glycid moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose, as well as glyceraldehyde. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilised as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z^2 . It should be understood that it is by no means intended to exclude other suitable raw materials. Z^2 preferably will be selected from the group consisting of $-\text{CH}_2-(\text{CHOH})_n-\text{CH}_2\text{OH}$, $-\text{CH}(\text{CH}_2\text{OH})-(\text{CHOH})_{n-1}-\text{CH}_2\text{H}$, $\text{CH}_2(\text{CHOH})_2(\text{CHOR}')(\text{CHOH})-\text{CH}_2\text{OH}$, where n is an integer from 1 to 5, inclusive, and R' is H or a cyclic mono- or polysaccharide, and alkoxylated derivatives thereof. As noted, most preferred are glycityls wherein n is 4, particularly $-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2\text{OH}$.

The most preferred polyhydroxy fatty acid amide has the formula $R^8(\text{CO})\text{N}(\text{CH}_3)\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}$ wherein R^8 is a C_6 - C_{19} straight chain alkyl or alkenyl group. In compounds of the above formula, $R^8-\text{CO}-\text{N}<$ can be, for example, cocoamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmiamide, tallowamide, etc.

Suitable oil derived nonionic surfactants for use herein include water soluble vegetable and animal-derived emollients such as triglycerides with a polyethyleneglycol chain inserted; ethoxylated mono and di-glycerides, polyethoxylated lanolins and ethoxylated butter derivatives. One preferred

class of oil-derived nonionic surfactants for use herein have the general formula below:



wherein n is from about 5 to about 200, preferably from about 20 to about 100, more preferably from about 30 to about 85, and wherein R comprises an aliphatic radical having on average from about 5 to 20 carbon atoms, preferably from about 7 to 18 carbon atoms.

Suitable ethoxylated oils and fats of this class include polyethyleneglycol derivatives of glyceryl cocoate, glyceryl caproate, glyceryl caprylate, glyceryl tallowate, glyceryl palmate, glyceryl stearate, glyceryl laurate, glyceryl oleate, glyceryl ricinoleate, and glyceryl fatty esters derived from triglycerides, such as palm oil, almond oil, and corn oil, preferably glyceryl tallowate and glyceryl cocoate.

Preferred for use in the pretreatment composition are polyethyleneglycol based polyethoxylated C₉-C₁₅ fatty alcohol nonionic surfactants containing an average of from about 5 to about 50 ethyleneoxy moieties per mole of surfactant.

Suitable polyethylene glycol based polyethoxylated C₉-C₁₅ fatty alcohols suitable for use herein include C₉-C₁₁ Pareth-3, C₉-C₁₁ Pareth-4, C₉-C₁₁ Pareth-5, C₉-C₁₁ Pareth-6, C₉-C₁₁ Pareth-7, C₉-C₁₁ Pareth-8, C₁₁-C₁₅ Pareth-3, C₁₁-C₁₅ Pareth-4, C₁₁-C₁₅ Pareth-5, C₁₁-C₁₅ Pareth-6, C₁₁-C₁₅ Pareth-7, C₁₁-C₁₅ Pareth-8, C₁₁-C₁₅ Pareth-9, C₁₁-C₁₅ Pareth-10, C₁₁-C₁₅ Pareth-11, C₁₁-C₁₅ Pareth-12, C₁₁-C₁₅ Pareth-13 and C₁₁-C₁₅ Pareth-14. PEG 40 hydrogenated castor oil is commercially available under the tradename Cremophor (RTM) from BASF. PEG 7 glyceryl cocoate and PEG 20 glyceryl laurate are commercially available from Henkel under the tradenames Cetiol (RTM) HE and Lamacit (RTM) GML 20 respectively. C₉-C₁₁ Pareth-8 is commercially available from Shell Ltd under the tradename Dobanol (RTM) 91-8. Particular preferred for use herein are polyethylene glycol ethers of

ceteryl alcohol such as Cetareth 25 which is available from BASF under the trade name Cremaphor A25.

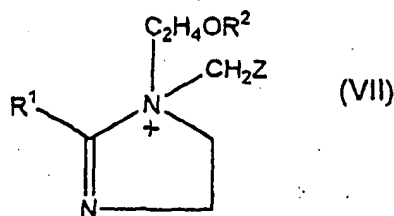
Also suitable for use in the pretreatment composition are nonionic surfactants derived from composite vegetable fats extracted from the fruit of the Shea Tree (*Butyrospermum Karkii* Kotschy) and derivatives thereof. Similarly, ethoxylated derivatives of Mango, Cocoa and Illipe butter may be used in compositions according to the invention. Although these are classified as ethoxylated nonionic surfactants it is understood that a certain proportion may remain as non-ethoxylated vegetable oil or fat.

Other suitable oil-derived nonionic surfactants include ethoxylated derivatives of almond oil, peanut oil, rice bran oil, wheat germ oil, linseed oil, jojoba oil, oil of apricot pits, walnuts, palm nuts, pistachio nuts, sesame seeds, rapeseed, cade oil, corn oil, peach pit oil, poppyseed oil, pine oil, castor oil, soybean oil, avocado oil, safflower oil, coconut oil, hazelnut oil, olive oil, grapeseed oil, and sunflower seed oil.

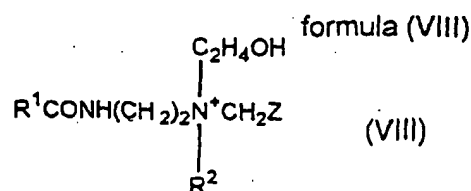
(iii) Amphoteric Surfactants

Amphoteric surfactants suitable for use in the compositions of the invention include:

(a) imidazolinium surfactants of formula (VII)



wherein R^1 is C_7 - C_{22} alkyl or alkenyl, R^2 is hydrogen or CH_2Z , each Z is independently CO_2M or $\text{CH}_2\text{CO}_2\text{M}$, and M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium; and/or ammonium derivatives of



13.

wherein R¹, R² and Z are as defined above;

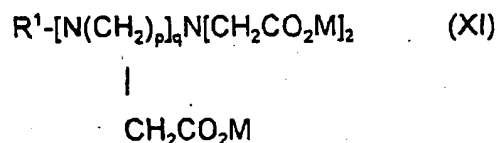
(b) aminoalkanoates of formula (IX)



iminodialkanoates of formula (X)



and iminopolyalkanoates of formula (XI)



wherein n, m, p, and q are numbers from 1 to 4, and R¹ and M are independently selected from the groups specified above; and

(c) mixtures thereof.

Suitable amphoteric surfactants of type (a) are marketed under the trade name Miranol and Empigen and are understood to comprise a complex mixture of species. Traditionally, the Miranols have been described as having the general formula (VII), although the CTFA Cosmetic Ingredient Dictionary, 3rd Edition indicates the non-cyclic structure (VIII) while the 4th Edition indicates yet another structural isomer in which R² is O-linked rather than N-linked. In practice, a complex mixture of cyclic and non-cyclic species is likely to exist and both definitions are given here for sake of completeness. Preferred for use herein, however, are the non-cyclic species.

Examples of suitable amphoteric surfactants of type (a) include compounds of formula XII and/or XIII in which R¹ is C₈H₁₇ (especially isocapryl), C₉H₁₉ and C₁₁H₂₃ alkyl. Especially preferred are the compounds in which R¹ is C₉H₁₉, Z is CO₂M and R² is H; the compounds in which R¹ is

$C_{11}H_{23}$, Z is CO_2M and R_2 is CH_2CO_2M ; and the compounds in which R^1 is $C_{11}H_{23}$, Z is CO_2M and R^2 is H.

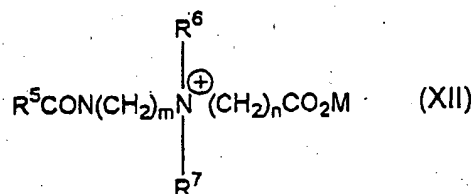
In CTFA nomenclature, materials suitable for use in the present invention include cocoamphocarboxypropionate, cocoamphocarboxy propionic acid, and especially cocoamphoacetate and cocoamphodiacetate (otherwise referred to as cocoamphocarboxyglycinate). Specific commercial products include those sold under the trade names of Ampholak 7TX (sodium carboxy methyl tallow polypropyl amine), Empigen CDL60 and CDR 60 (Albright & Wilson), Miranol H2M Conc. Miranol C2M Conc. N.P., Miranol C2M Conc. O.P., Miranol C2M SF, Miranol CM Special (Rhône-Poulenc); Alkateric 2CIB (Alkaril Chemicals); Amphoterger W-2 (Lonza, Inc.); Monateric CDX-38, Monateric CSH-32 (Mona Industries); Rewoteric AM-2C (Rewo Chemical Group); and Schercotic MS-2 (Scher Chemicals). Further examples of amphoteric surfactants suitable for use herein include Octoxynol-1 (RTM), polyoxyethylene (1) octylphenyl ether; Nonoxynol-4 (RTM), polyoxyethylene (4) nonylphenyl ether and Nonoxynol-9, polyoxyethylene (9) nonylphenyl ether.

It will be understood that a number of commercially-available amphoteric surfactants of this type are manufactured and sold in the form of electroneutral complexes with, for example, hydroxide counterions or with anionic sulfate or sulfonate surfactants, especially those of the sulfated C_8 - C_{18} alcohol, C_8 - C_{18} ethoxylated alcohol or C_8 - C_{18} acyl glyceride types. Note also that the concentrations and weight ratios of the amphoteric surfactants are based herein on the uncomplexed forms of the surfactants, any anionic surfactant counterions being considered as part of the overall anionic surfactant component content.

Examples of preferred amphoteric surfactants of type (b) include N-alkyl polytrimethylene poly-, carboxymethylamines sold under the trade names Ampholak X07 and Ampholak 7CX by Berol Nobel and also salts, especially the triethanolammonium salts and salts of N-lauryl-beta-amino propionic acid and N-lauryl-imino-dipropionic acid. Such materials are sold under the trade name Deriphath by Henkel and Mirataine by Rhône-Poulenc.

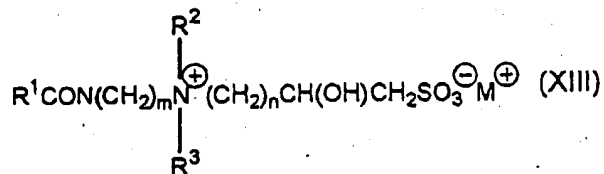
(iv) Zwitterionic Surfactants

Water-soluble auxiliary zwitterionic surfactants suitable for inclusion in the compositions of the present invention include alkyl betaines of the formula $R^5R^6R^7N^+(CH_2)_nCO_2M$ and amido betaines of the formula (XII) below:



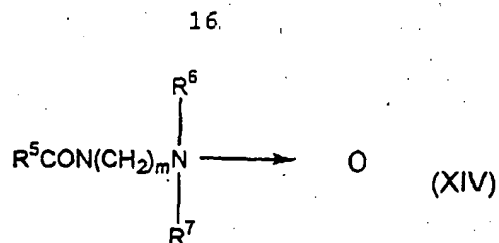
wherein R^5 is C_{11} - C_{22} alkyl or alkenyl, R^6 and R^7 are independently C_1 - C_3 alkyl, M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium, and n, m are each numbers from 1 to 4. Preferred betaines include cocoamidopropyldimethylcarboxymethyl betaine, laurylamidopropyldimethylcarboxymethyl betaine and Tego betaine (RTM).

Water-soluble auxiliary sultaine surfactants suitable for inclusion in the pretreatment composition includes alkyl sultaines of the formula (XIII) below:



wherein R^1 is C_7 to C_{22} alkyl or alkenyl, R^2 and R^3 are independently C_1 to C_3 alkyl, M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium and m and n are numbers from 1 to 4. Preferred for use herein is coco amido propylhydroxy sultaine.

Water-soluble auxiliary amine oxide surfactants suitable for inclusion in the compositions of the present invention include alkyl amine oxide $R^5R^6R^7NO$ and amido amine oxides of the formula (XIV) below:



wherein R_5 is C_{11} to C_{22} alkyl or alkenyl, R^6 and R^7 are independently C_1 to C_3 alkyl, M is H , alkali metal, alkaline earth metal, ammonium or alkanolammonium and m is a number from 1 to 4. Preferred amine oxides include cocoamidopropylamine oxide, lauryl dimethyl amine oxide and myristyl dimethyl amine oxide.

(v) Cationic Surfactants

Cationic surfactants suitable for inclusion in the compositions of the present invention include Polyquaternium-4 (Celquat H-100; L200--supplier National Starch); Polyquaternium-10 (Celquat SC-240C; SC-230 M--supplier National Starch); (UCARE polymer series--JR-125, JR-400, LR-400, LR-30M, LK, supplier Amerchol); Polyquaternium-11 (Gafquat 734; 755N--supplier ISP); Polyquaternium-16 (Luviquat FC 370; FC550; FC905; HM-552 supplier by BASF); PVP/Dimethylaminoethylmethacrylate (Copolymer 845; 937; 958--ISP supplier); Vinyl Caprolactam/PVP/Dimethylaminoethyl Methacrylate copolymer (Gaffix VC-713; H2OLD EP-1--supplier ISP); Chitosan (Kytamer L; Kytamer PC--supplier Amerchol); Polyquaternium-7 (Merquat 550--supplier Calgon); Polyquaternium-18 (Mirapol AZ-1 supplied by Rhone-Poulenc); Polyquaternium-24 (Quatrisoft Polymer LM-200--supplier Amerchol); Polyquaternium-28 (Gafquat HS-100--supplier ISP); Polyquaternium-46 (Luviquat Hold--supplier BASF); and, Chitosan Glycolate (Hydagen CMF; CMFP--supplier Henkel); Hydroxyethyl Cetyldimonium Phosphate (Luviquat Mono CP--supplier BASF); and, Guar Hydroxylpropyl Trimonium Chloride (Jaguar C series -13S, -14S, -17, 162, -2000, Hi-CARE 1000--supplier Rhone-Poulenc).

Preferred cationic polymers are Polyquaternium-4; Polyquaternium-10; Polyquaternium-11; Polyquaternium-16; PVP/Dimethylaminoethyl Vinyl Caprolactam/PVP/Dimethylaminoethyl Methacrylate copolymer; and, Chitosan.

5 Optional Materials

A number of additional optional materials can be added to the pretreatment composition, each at a level of from about 0.001% to about 5%, preferably from about 0.01% to about 3%, more preferably from about 0.05% to about 2% by weight of composition. Such materials include proteins and polypeptides and derivatives thereof; water-soluble or solubilizable preservatives such as DMDM Hydantoin, Germall 115, methyl, ethyl, propyl and butyl esters of hydroxybenzoic acid, EDTA, Euxyl (RTM) K400, natural preservatives such as benzyl alcohol, potassium sorbate and bisababol, benzoic acid, sodium benzoate and 2-phenoxyethanol; antioxidants such as sodium sulphite, hydroquinone, sodium bisulphite, sodium metabisulphite and thyoglycolic acid, sodium dithionite, erythrolic acid and other mercaptans; coloring agent removers such as oxalic acid, sulphated castor oil, salicylic acid and sodium thiosulphate; H₂O₂ stabilisers such as tin compounds such as sodium stannate, stannic hydroxide and stannous octoate, acetanilide, phenacetin colloidal silica such as magnesium silicate, oxyquinoline sulphate, sodium phosphate, and tetrasodium pyrophosphate; and -hydroxybenzoates; moisturising agents such as hyaluronic acid, chitin, and starch-grafted sodium polyacrylates such as Sanwet (RTM) IM-1000, IM-1500 and IM-2500 available from Celanese Superabsorbent Materials, Portsmouth, VA, USA and described in US-A-4,076,663 as well as methyl cellulose, starch, higher fatty alcohols, paraffin oils, fatty acids and the like; solvents; anti-bacterial agents such as Oxeco (phenoxy isopropanol); low temperature phase modifiers such as ammonium ion sources (e.g. NH₄ Cl); viscosity control agents such as magnesium sulfate and other electrolytes; quaternary amine compounds such as distearyl-, dilauryl-, di-hydrogenated beef tallow-, dimethyl ammonium chloride, dicetyldiethyl ammoniummethylsulphate, ditallowdimethyl ammonium methylsulphate, disoya

10
15
20
25
30

dimethyl ammonium chloride and dicoco dimethyl ammonium chloride; hair conditioning agents such as silicones, higher alcohols, cationic polymers and the like; enzyme stabilisers such as water soluble sources of calcium or borate species; coloring agents; TiO_2 and TiO_2 -coated mica; perfumes and perfume solubilizers; and zeolites such as Valfour BV400 and derivatives thereof and $\text{Ca}^{2+}/\text{Mg}^{2+}$ sequestrants such as polycarboxylates, amino polycarboxylates, polyphosphonates, amino polyphosphonates etc. and water softening agents such as sodium citrate.

Another essential feature of the present invention is the provision of a second, hair coloring or bleaching step, which involves treating the hair with a color altering composition having a pH less than that of the pretreatment composition.

It is postulated that upon the application of the color altering composition to the hair whilst the pretreatment composition remains on the hair, the pH of the combination of compositions on the hair gradually decreases due to the pH of the second step composition. The initial high pH (immediately after the application of the color altering composition) has the effect of promoting the reaction of the coloring and/or bleaching components of the color altering composition but as the pH decreases, damage to the hair is limited (damage is increased under high pH conditions).

The color altering composition generally contains one or more coloring agents. Coloring agents are components which apply a color to the hair. The coloring agents may be oxidative or non-oxidative or a combination of these, but are preferably oxidative. The color altering composition usually also contains an oxidising agent, and optional additional components which may or may not be active ingredients. Thus, the color altering composition may contain, in addition to a mixture of active oxidising agents and one or more coloring agents, other ingredients such as oxidising aids, sequestrants, stabilisers, thickeners, buffers, carriers, surfactants, solvents, antioxidants, polymers, and conditioners.

The color altering composition can be a hair lightening composition. Such compositions can contain one or more coloring agents that produce

colors which are lighter than the initial hair color, preferably with an oxidising agent. They may contain no coloring components at all but simply an oxidising agent to lighten the hair. In general, however, they contain at least some coloring agent.

5 The color altering compositions utilised in the present invention preferably have a pH in the range of from about 1 to 9, more preferably about 1.5 to about 7, more preferably from about 2 to about 6, in particular from about 2.5 to about 5.8 and especially from about 3.5 to about 5.5.

10 Several different pH modifiers can be used to adjust the pH of the color altering composition utilised in the present method.

 This pH adjustment can be effected by using well known acidifying agents in the field of treating keratinous fibres, and in particular human hair, such as inorganic and organic acids such as hydrochloric acid, tartaric acid, citric acid, succinic acid, phosphoric acid and carboxylic or sulphonic acids
15 such as ascorbic acid, acetic acid, lactic acid, sulphuric acid, formic acid, ammonium sulphate and sodium dihydrogenphosphate /phosphoric acid, disodium hydrogenphosphate /phosphoric acid, potassium chloride /hydrochloric acid, potassium dihydrogen phthalate/ hydrochloric acid, sodium citrate / hydrochloric acid, potassium dihydrogen citrate /hydrochloric
20 acid, potassium dihydrogencitrate/ citric acid, sodium citrate / citric acid, sodium tartarate/ tartaric acid, sodium lactate/ lactic acid, sodium acetate/ acetic acid, disodium hydrogenphosphate/ citric acid and sodium chloride/ glycine / hydrochloric acid, succinic acid and mixtures thereof.

 Examples of alkaline buffering agents are ammonium hydroxide,
25 ethylamine, dipropylamine, triethylamine and alkanediamines such as 1,3-diaminopropane, anhydrous alkaline alkanolamines such as, mono or di-ethanolamine, preferably those which are completely substituted on the amine group such as dimethylaminoethanol, polyalkylene polyamines such as diethylenetriamine or a heterocyclic amine such as morpholine as well as
30 the hydroxides of alkali metals, such as sodium and potassium hydroxide, hydroxides of alkali earth metals, such as magnesium and calcium hydroxide, basic amino acids such as L-arginine, lysine, alanine, leucine,

iso-leucine, oxylysine and histidine and alkanolamines such as dimethylaminoethanol and aminoalkylpropanediol and mixtures thereof.

In a second aspect of the invention, the method of altering hair color utilizes a color altering composition having a pH in the range 1 to 6, preferably less than 6. In this aspect of the invention the pretreatment composition may remain on the hair during application of the color altering composition, although, in a preferred embodiment the pretreatment is rinsed from the hair prior to application of the color altering composition.

In the second aspect of the invention however, any of the other features relevant to the first aspect of the invention may be present.

The compositions used in the methods according to the present invention may be provided as kits comprising of a number of separate components. In a preferred embodiment the kits comprise at least two components.

It is essential that the pretreatment composition is presented separately from the color altering composition.

In a preferred embodiment, the pretreatment composition may be presented in a form selected from foams, aerosol foams / mousses, conditioners, shampoos, tonics, aqueous sprays and gels. Most preferably the pretreatment composition is presented as a foam.

A preferred kit comprises two components. The first component is presented separately (ie. not attached) from the second and comprises the pretreatment composition. The second component comprises a color altering composition containing an oxidative hair coloring agent and oxidising composition, preferably containing a peroxygen bleach oxidising agent.

It is important that the color altering compositions be in a form which is easy and convenient to prepare and use by the consumer, since the oxidising agent must remain in contact with the hair for a certain period of time and not run or drip off of the hair, possibly causing eye or skin irritation.

To address the above, the color altering compositions of the present invention can be provided as a single pack or as a kit comprising separately

packaged components. This latter feature allows one to maintain stability of the coloring composition. This also allows the hair color altering composition components to either be mixed by the user immediately prior to application to the hair, or mixed and stored for future use, or mixed and part of the mixture used and the remainder stored for future use. Color altering components can be delivered from a single package having multi-compartments to keep each component separate until it is mixed. Suitable single packages having multiple compartments include those disclosed in WO99/26508, WO99/26509, WO99/26510, WO99/26511 and WO99/26596 and these are the preferred packaging used for the present invention.

In another embodiment, the packaging may comprise a multi-compartment, aerosol packaging or a delaminating bottle packaging.

The color altering compositions according to the present invention may be provided to the consumer in the form of a single component package. Such a single pack comprises a single solution containing the oxidising agent, and the hair coloring agent. The single solution is applied directly to the hair by the consumer subsequent to the application of the pretreatment composition, thereby providing a simple, fast, easy to use, 'no-mess' hair coloring system. A further advantage of such a single component system is that it can be stored and re-used i.e., a single package may contain enough coloring composition for several applications over time.

However, the oxidative hair coloring agent and oxidising agents are preferably kept apart from one another until application to the hair is undertaken. This may be accomplished by the provision of a compartmentalised packaging. This packaging contains the oxidative hair coloring agent and oxidising composition but does not allow the compositions to contact each other until the compositions are mixed. Mixing is usually undertaken by the user immediately prior to application to the hair.

The components can also be mixed and the resulting composition can be stored for future use or part of the resulting composition can be used and the rest of the composition stored for future use.

The kit comprises instructions for use of the compositions disclosed herein. These include instructions to carry out any of the steps described above.

Oxidising Agents

5 The color altering compositions used in the methods of the invention may comprise an oxidising agent, which may be an inorganic or organic oxidising agent. The oxidising agent is preferably present at a level of from about 0.01% to about 10%, preferably from about 0.01% to about 6%, more preferably from about 1% to about 4% by weight of composition.

10 In a particularly preferred aspect the color altering compositions utilised in the present invention comprise from about 0.0003 moles (per 100g of composition) to less than about 0.09 moles (per 100g of composition) of an inorganic peroxygen based oxidising agent.

Inorganic Oxidising Agents

15 A preferred oxidising agent for use herein is an inorganic peroxygen oxidising agent.

The inorganic peroxygen oxidising agent should be safe and effective for use in the methods herein. Preferably, the inorganic peroxygen oxidising agents suitable for use herein will be soluble in the compositions used in the methods according to the present invention when in liquid form or in the form
20 intended to be used. Preferably, inorganic peroxygen oxidising agents suitable for use herein will be water-soluble. Water soluble oxidising agents as defined herein means agents which have a solubility to the extent of about 10g in 1000ml of deionised water at 25°C ("Chemistry" C. E. Mortimer, 5th Edn. p277).
25

The inorganic peroxygen oxidising agents useful herein are generally inorganic peroxygen materials capable of yielding peroxide in an aqueous solution. Inorganic peroxygen oxidising agents are well known in the art and include hydrogen peroxide, inorganic alkali metal peroxides such as sodium
30 periodate, sodium perbromate and sodium peroxide, and inorganic perhydrate salt oxidising compounds, such as the alkali metal salts of perborates, percarbonates, perphosphates, persilicates, persulphates and

the like. These inorganic perhydrate salts may be incorporated as monohydrates, tetrahydrates etc. Mixtures of two or more of such inorganic peroxygen oxidising agents can be used if desired. While alkali metal bromates and iodates are suitable for use herein the bromates are preferred.

5 Highly preferred for use in the compositions used in the methods according to the present invention is hydrogen peroxide.

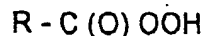
It has been found that by using the methods of the present invention, it is possible to deliver effective hair bleaching and coloring without needing to use ammonia, hence there being no ammonia related odor or skin
10 irritation negatives associated with these compositions.

In preferred compositions used in the methods according to the present invention the inorganic peroxygen oxidising agent is present at a level of from about 0.01% to less than about 6%, preferably from about 0.01% to about 4%, more preferably from about 1% to about 4%, more
15 preferably from about 2% to about 3% by weight of color composition.

Preformed organic peroxyacid

The color altering compositions used in the methods according to the present invention may instead or in addition to the inorganic peroxygen oxidising agent(s), comprise one or more preformed organic peroxyacid
20 oxidising agents.

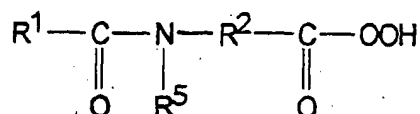
Suitable organic peroxyacid oxidising agents for use in the coloring compositions according to the present invention have the general formula:



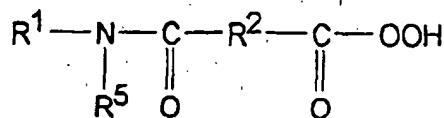
25 wherein R is selected from saturated or unsaturated, substituted or unsubstituted, straight or branched chain, alkyl, aryl or alkaryl groups with from 1 to 14 carbon atoms.

A class of organic peroxyacid compounds suitable for use herein are the amide substituted compounds of the following general formulae:

30



or



- 5 wherein R¹ is, a saturated or unsaturated alkyl or alkaryl group, or an aryl group, having from 1 to 14 carbon atoms, R² is, a saturated or unsaturated alkyl or alkaryl group, or an aryl group, having from 1 to 14 carbon atoms, and R⁵ is H or, a saturated or unsaturated alkyl or alkaryl group, or an aryl group, having from 1 to 10 carbon atoms. Amide substituted organic
 10 peroxyacid compounds of this type are described in EP-A-0,170,386.

Other suitable organic peroxyacid oxidising agents include peracetic, pernanoic, nonylamidoperoxyacaproic acid (NAPCA), perbenzoic, m-chloroperbenzoic, di-peroxy-isophthalic, mono-peroxyphthalic, peroxyauric, hexanesulphonyl peroxy propionic, N,N-phthaloylamino peroxyacaproic,
 15 monoper succinic, nonanoyloxybenzoic, dodecanedioyl-monoperoxybenzoic, nonylamide of peroxyadipic acid, diacyl and tetraacylperoxides, especially diperoxydodecanedioic acid, diperoxytetradecanedioic acid and diperoxyhexadecanedioic acid and derivatives thereof. Mono- and
 20 diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylamino peroxycaproic acid and derivatives thereof are also suitable for use herein.

The preformed organic peroxyacid oxidising agents should be safe and effective for use in the compositions herein. Preferably, the preformed organic peroxyacid oxidising agents suitable for use herein will be soluble in
 25 the compositions according to the present invention when in liquid form and in the form intended to be used. Preferably, organic peroxyacid oxidising agents suitable for use herein will be water-soluble. Water-soluble preformed organic peroxyacid oxidising agents as defined herein means agents which have a solubility to the extent of about 10g in 1000ml of
 30 deionised water at 25°C ("Chemistry" C. E. Mortimer. 5th Edn. p277).

The preferred peroxyacid materials suitable for use herein are selected from peracetic and pernanoic acids and mixtures thereof.

The preformed organic peroxyacid oxidising agent, where present, is preferably present at a level of from about 0.01% to about 8%, more preferably from about 0.1% to about 6%, most preferably from about 0.2% to about 4%, and especially from about 0.3% to about 3% by weight of the hair coloring composition.

When both an inorganic peroxygen oxidising agent and a preformed organic peroxy acid are present in the color altering compositions herein, the weight ratio of the inorganic peroxygen oxidising agent to the preformed organic peroxy acid is preferably in the range of from about 0.0125:1 to about 500:1, more preferably from about 0.0125:1 to about 50:1.

In addition to the inorganic peroxygen oxidising agents and the preformed organic peroxyacid oxidising agents suitable for use herein, the color altering compositions according to the present invention may optionally comprise additional organic peroxides such as urea peroxide, melamine peroxide and mixtures thereof. The level of organic peroxide, where present, is from about 0.01% to about 3%, preferably from about 0.01% to about 2%, more preferably from about 0.1% to about 1.5% and most preferably from about 0.2% to about 1% by weight of composition.

Hair Coloring Agents

The color altering compositions utilized in the present invention include as an essential feature an oxidative or non-oxidative hair coloring agent. Such hair coloring agents are used in combination with the oxidising agent to formulate permanent, demi-permanent, semi-permanent or temporary hair coloring compositions.

Most preferably the coloring altering compositions comprise an oxidative hair coloring agent, and contain substantially no non-oxidative hair coloring agents.

Permanent hair coloring compositions as defined herein are compositions which once applied to the hair are substantially resistant to wash-out. Demi-permanent hair coloring compositions as defined herein are compositions which are substantially removed from the hair after up to 24 washes. Semi-permanent hair coloring compositions as defined herein are

compositions which once applied to the hair are substantially removed from the hair after up to 10 washes. Temporary hair coloring compositions as defined herein are compositions which once applied to the hair are substantially removed from the hair after up to 2 washes. These different
5 types of hair coloring compositions can be formulated via the specific combination of oxidant and/or coloring agents at different levels and ratios. Wash out as defined herein is the process by which hair color is removed from the hair over time during normal hair cleansing regimen. Washfastness means the resistance of the colored hair to wash out.

10 Oxidative hair coloring agents

A preferred hair coloring agent herein is an oxidative hair coloring agent. The concentration of each oxidative hair coloring agent in the coloring compositions according to the present invention is preferably from about 0.001% to about 3% by weight, more preferably from about 0.01% to
15 about 2% by weight.

The total combined level of oxidative hair coloring agents in the compositions according to the present invention is from about 0.001% to about 5%, preferably from about 0.01% to about 4%, more preferably from about 0.1% to about 3%, most preferably from about 0.1% to about 2% by
20 weight.

Any oxidative hair coloring agent can be used in the compositions according to the present invention. Typically, but without intending to be limited thereby, oxidative hair coloring agents, consist essentially of at least two components, which are collectively referred to as dye forming
25 intermediates (or precursors). Dye forming intermediates can react in the presence of a suitable oxidant to form a colored molecule.

The dye forming intermediates used in oxidative hair colorants include: aromatic diamines, aminophenols, various heterocycles, phenols, naphthols and their various derivatives. These dye forming intermediates can
30 be broadly classified as; primary intermediates and secondary intermediates. Primary intermediates, which are also known as oxidative dye precursors, are chemical compounds which become activated upon oxidation and can

then react with each other and/or with couplers to form colored dye complexes. The secondary intermediates, also known as color modifiers or couplers, are generally colorless molecules which can form colors in the presence of activated precursors/primary intermediates, and are used with
5 other intermediates to generate specific color effects or to stabilise the color.

Primary intermediates suitable for use in the compositions and processes herein include: aromatic diamines, polyhydric phenols, amino phenols and derivatives of these aromatic compounds (e.g., N-substituted derivatives of the amines, and ethers of the phenols). Such primary
10 intermediates are generally colorless molecules prior to oxidation.

It is believed that the process by which color is generated from these primary intermediates and secondary coupler compounds generally includes a stepwise sequence whereby the primary intermediate can become activated (by oxidation), and then enjoins with a coupler to give a dimeric,
15 conjugated colored species, which in turn can enjoin with another 'activated' primary intermediate to produce a trimeric conjugated colored molecule.

Oxidative Dye Precursors

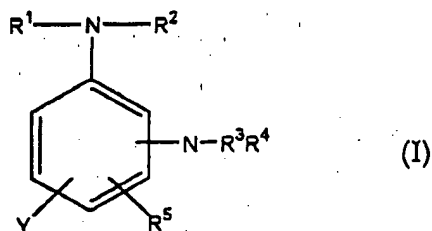
In general terms, oxidative dye primary intermediates include those monomeric materials which, on oxidation, form oligomers or polymers having
20 extended conjugated systems of electrons in their molecular structure. Because of the new electronic structure, the resultant oligomers and polymers exhibit a shift in their electronic spectra to the visible range and appear colored. For example, oxidative primary intermediates capable of forming colored polymers include materials such as aniline, which has a
25 single functional group and which, on oxidation, forms a series of conjugated imines and quinoid dimers, trimers, etc. ranging in color from green to black. Compounds such as p-phenylenediamine, which has two functional groups, are capable of oxidative polymerization to yield higher molecular weight colored materials having extended conjugated electron systems. Oxidative
30 dyes known in the art can be used in the compositions according to the present invention. A representative list of primary intermediates and secondary couplers suitable for use herein is found in Sagarin, "Cosmetic

Science and Technology," Interscience, Special Ed. Vol. 2 pages 308 to 310. It is to be understood that the primary intermediates detailed below are only by way of example and are not intended to limit the compositions and processes herein.

5 The typical aromatic diamines, polyhydric phenols, amino phenols, and derivatives thereof, described above as primary intermediates can also have additional substituents on the aromatic ring, e.g. halogen, aldehyde, carboxylic acid, nitro, sulfonic acid and substituted and unsubstituted hydrocarbon groups, as well as additional substituents on the amino nitrogen
10 and on the phenolic oxygen, e.g. substituted and unsubstituted alkyl and aryl groups.

Examples of suitable aromatic diamines, amino phenols, polyhydric phenols and derivatives thereof, respectively, are compounds having the general formulas (I), (II) and (III) below:

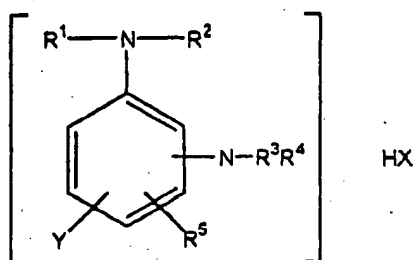
15



20

OR

25



wherein Y is hydrogen, halogen, (e.g. fluorine, chlorine, bromine or iodine),
30 nitro, amino, hydroxyl,

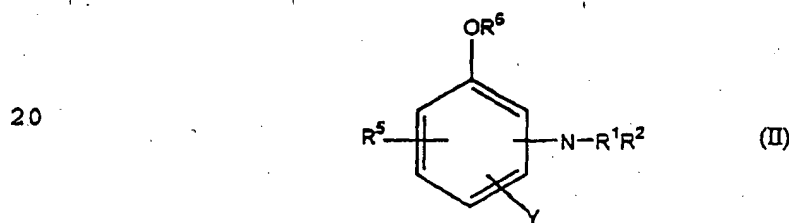


-COOM or -SO₃M (where M is hydrogen or an alkali or alkaline earth metal, ammonium, or substituted ammonium wherein one or more hydrogens on the ammonium ion is replaced with a 1 to 3 carbon atom alkyl or hydroxyalkyl radical), wherein R¹, R², R³ and R⁴ are the same or different from each other and are selected from the group consisting of hydrogen, C₁ to C₄ alkyl or alkenyl and C₆ to C₉ aryl, alkaryl or aralkyl, and R⁵ is hydrogen, C₁ to C₄ unsubstituted or substituted alkyl or alkenyl wherein the substituents are selected from those designated as Y, above, or C₆ to C₉ unsubstituted or substituted aryl, alkaryl or aralkyl wherein the substituents are selected from those defined as Y, above. Since the precursors of formula (I) are amines, they can be used herein in the form of peroxide-compatible salts, as noted, wherein X represents peroxide-compatible anions of the type herein before detailed. The general formula of the salt indicated is to be understood to encompass those salts having mono-, di-, and tri-negative anions.

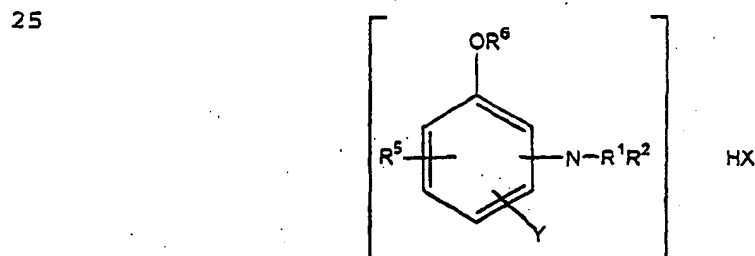
Specific examples of formula (I) compounds are: o-phenylenediamine, m-phenylenediamine, p-phenylenediamine, 2-chloro-p-phenylenediamine, 2-iodo-p-phenylenediamine, 4-nitro-o-phenylenediamine, 2-nitro-p-phenylenediamine, 1,3,5-triaminobenzene, 2-hydroxy-p-phenylenediamine, 2,4-diaminobenzoic acid, sodium 2,4-diaminobenzoate, calcium di-2,4-diaminobenzoate, ammonium 2,4-diaminobenzoate, trimethylammonium 2,4-diaminobenzoate, tri-(2-hydroxyethyl)ammonium 2,4-diaminobenzoate, 2,4-diaminobenzaldehyde carbonate, 2,4-diaminobenzenesulfonic acid, potassium 2,4-diaminobenzenesulfonate, N,N-diisopropyl-p-phenylenediamine bicarbonate, N,N-dimethyl-p-phenylenediamine, N-ethyl-N'-(2-propenyl)-p-phenylenediamine, N-phenyl-p-phenylenediamine, N-phenyl-N-benzyl-p-phenylenediamine, N-ethyl-N'-(3-ethylphenyl)-p-phenylenediamine, 2,4-toluenediamine, 2-ethyl-p-phenylenediamine, 2-(2-bromoethyl)-p-phenylenediamine, 2-phenyl-p-phenylenediamine laurate, 4-(2,5-diaminophenyl)benzaldehyde, 2-benzyl-p-phenylenediamine acetate, 2-(4-nitrobenzyl)-p-phenylenediamine, 2-(4-methylphenyl)-p-phenylenediamine, 2-(2,5-diaminophenyl)-5-methylbenzoic acid, methoxyparaphenylenediamine, dimethyl-p-phenylenediamine, 2,5-

dimethylpara-phenylenediamine, 2-methyl-5-methoxy-para-phenylenediamine, 2,6-methyl-5-methoxy-para-phenylenediamine, 3-methyl-4-amino-N,N-diethylaniline, N,N-bis(-hydroxyethyl)-para-phenylenediamine, 3-methyl-4-amino-N,N-bis(-hydroxyethyl)aniline, 3-chloro-4-amino-N,N-bis(-hydroxyethyl)aniline, 4-amino-N-ethyl-N-(carbamethyl)aniline, 3-methyl-4-amino-N-ethyl-N-(carbamethyl)aniline, 4-amino-N-ethyl-(-piperidonoethyl)aniline, 3-methyl-4-amino-N-ethyl-(-piperidonoethyl)aniline, 4-amino-N-ethyl-N-(-morpholinoethyl)aniline, 3-methyl-4-amino-N-ethyl-N-(-morpholinoethyl)aniline, 4-amino-N-ethyl-N-(-acetylaminoethyl)aniline, 4-amino-N-(-methoxyethyl) aniline, 3-methyl-4-amino-N-ethyl-N-(-acetylaminoethyl) aniline, 4-amino-N-ethyl-N-(-mesylaminoethyl) aniline, 3-methyl-4-amino-N-ethyl-N-(-mesylaminoethyl) aniline, 4-amino-N-ethyl-N-(-sulphoethyl) aniline, 3-methyl-4-amino-N-ethyl-N-(-sulphoethyl) aniline, N-(4-aminophenyl)morpholine, N-(4-aminophenyl)piperidine, 2,3-dimethyl-p-phenylenediamine, isopropyl-p-phenylenediamine, N,N-bis-(2-hydroxyethyl)-p-phenylenediamine sulphate.

Compounds having the general structure (II) are as follows:



OR



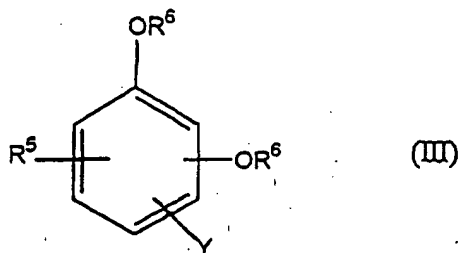
30

where X and Y are the same as in formula (I), R¹ and R² can be the same or different from each other and are the same as in formula (I), R⁵ is the same

as in formula (I) and R⁶ is hydrogen or C₁ to C₄ substituted or unsubstituted alkyl or alkenyl wherein the substituents are selected from those defined as Y in formula (I).

Specific examples of formula (II) compounds are:

- 5 o-aminophenol, m-aminophenol, p-aminophenol, 2-iodo-p-aminophenol, 2-nitro-p-aminophenol, 3,4-dihydroxyaniline, 3,4-diaminophenol, chloroacetate, 2-hydroxy-4-aminobenzoic acid, 2-hydroxy-4-aminobenzaldehyde, 3-amino-4-hydroxybenzenesulfonic acid, N,N-diisopropyl-p-aminophenol, N-methyl-N-(1-propenyl)-p-aminophenol, N-phenyl-N-benzyl-p-aminophenol sulphate, N-methyl-N-(3-ethylphenyl)-p-aminophenol, 2-nitro-5-ethyl-p-aminophenol, 2-nitro-5-(2-bromoethyl)-p-aminophenol, (2-hydroxy-5-aminophenyl)acetaldehyde, 2-methyl-p-aminophenol, (2-hydroxy-5-aminophenyl)acetic acid, 3-(2-hydroxy-5-aminophenyl)-1-propene, 3-(2-hydroxy-5-aminophenyl)-2-chloro-1-propene, 15 2-phenyl-p-aminophenol palmitate, 2-(4-nitrophenyl)-p-aminophenol, 2-benzyl-p-aminophenol, 2-(4-chlorobenzyl-p-aminophenol perchlorate, 2-(4-methylphenyl)-p-aminophenol, 2-(2-amino-4-methylphenyl)-p-aminophenol, p-methoxyaniline, 2-bromoethyl-4-aminophenyl ether phosphate, 2-nitroethyl-4-aminophenyl ether bromide, 2-aminoethyl-4-aminophenyl ether, 20 2-hydroxyethyl-4-aminophenyl ether, (4-aminophenoxy)acetaldehyde, (4-aminophenoxy)acetic acid, (4-aminophenoxy)methanesulfonic acid, 1-propenyl-4-aminophenyl ether isobutyrate, (2-chloro)-1-propenyl-4-aminophenyl ether, (2-nitro)-1-propenyl-4-aminophenyl ether, (2-amino)-propenyl-4-aminophenyl ether, (2-hydroxy)-1-propenyl-4-aminophenyl ether, 25 N-methyl-p-aminophenol, 3-methyl-4-aminophenol, 2-chloro-4-aminophenol, 3-chloro-4-aminophenol, 2,6-dimethyl-4-aminophenol, 3,5-dimethyl-4-aminophenol, 2,3-dimethyl-4-aminophenol, 2,5-dimethyl-4-aminophenol, 2-hydroxymethyl-4-aminophenol, 3-hydroxymethyl-4-aminophenol, 2,6-dichloro-4-aminophenol, 2,6-dibromo-4-aminophenol and 2-bromo-4-aminophenol. 30



where Y is the same as in formula (I), R^1 and R^2 can be the same or different from each other and are the same as in formula (I), R^5 is the same as in formula (I) and R^6 is hydrogen or C_1 to C_4 substituted or unsubstituted alkyl or alkenyl wherein the substituents are selected from those defined as Y in formula (I).

Specific examples of formula (III) compounds are:

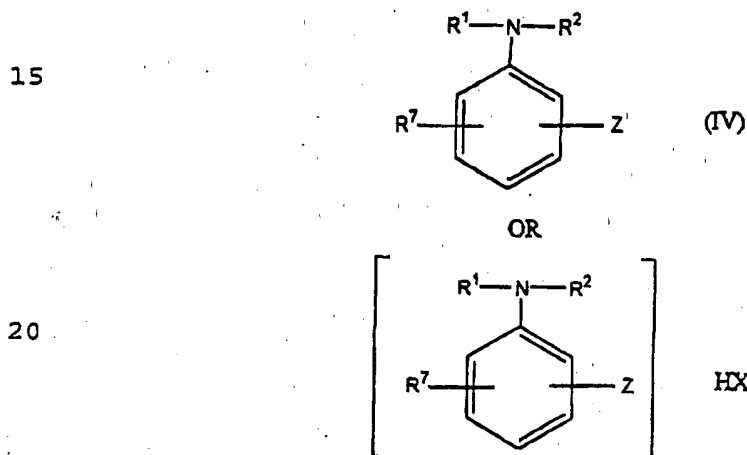
o-hydroxyphenol (catechol), m-hydroxyphenol (resorcinol), p-hydroxyphenol (hydroquinone), 4-methoxyphenol, 2-methoxyphenol, 4-(2-chloroethoxy) phenol, 4-(2-propenoxy) phenol, 4-(3-chloro-2-propenoxy) phenol, 2-chloro-4-hydroxyphenol (2-chlorohydroquinone), 2-nitro-4-hydroxyphenol (2-nitrohydroquinone), 2-amino-4-hydroxyphenol, 1,2,3-trihydroxybenzene (pyrogallol), 2,4-dihydroxybenzaldehyde, 3,4-dihydroxybenzoic acid, 2,4-dihydroxybenzenesulfonic acid, 3-ethyl-4-hydroxyphenol, 3-(2-nitroethyl)-4-hydroxyphenol, 3-(2-propenyl)-4-hydroxyphenol, 3-(3-chloro-2-propenyl)-4-hydroxyphenol, 2-phenyl-4-hydroxyphenol, 2-(4-chlorophenyl)-4-hydroxyphenol, 2-benzyl-4-hydroxyphenol, 2-(2-nitrophenyl)-4-hydroxyphenol, 2-(2-methylphenyl)-4-hydroxyphenol, 2-(2-methyl-4-chlorophenyl)-4-hydroxyphenol, 3-methoxy-4-hydroxy-benzaldehyde, 2-methoxy-4-(1-propenyl)phenol, 4-hydroxy-3-methoxycinnamic acid, 2,5-dimethoxyaniline, 2-methylresorcinol, alpha naphthol and salts thereof.

Secondary coupling compounds which are suitable for inclusion in the coloring compositions and processes herein before described include certain aromatic amines and phenols and derivatives thereof which do not produce color singly, but which modify the color, shade or intensity of the colors developed by the primary oxidized dye intermediates. Certain aromatic amines and phenolic compounds, and derivatives thereof, including some

aromatic diamines and polyhydric phenols of the types described by formulas (I), (Ia), (Ib), (II) and (III) above, but which are well known in the art not to be suitable primary intermediates, are suitable as couplers herein. Polyhydric alcohols are also suitable for use as couplers herein.

5 The aromatic amines and phenols and derivatives described above as couplers can also have additional substituents on the aromatic ring, e.g., halogen, aldehyde, carboxylic acid, nitro, sulfonyl and substituted and unsubstituted by hydrocarbon groups, as well as additional substituents on the amino nitrogen, or phenolic oxygen, e.g. substituted and unsubstituted
10 alkyl and aryl groups. Again, peroxide-compatible salts thereof are suitable for use herein.

Examples of aromatic amines, phenols and derivatives thereof are compounds of the general formulas (IV) and (V) below:



wherein Z is hydrogen, C₁ to C₃ alkyl, halogen (e.g. fluorine, chlorine,
25 bromine or iodine) nitro,



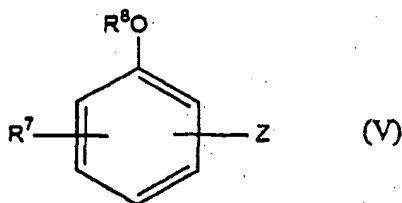
-COOM or SO₃M, (where M is hydrogen or an alkali or alkaline earth metal, ammonium or substituted ammonium wherein one or more hydrogens on the
30 ammonium ion is replaced with a 1 to 3 carbon atom alkyl or hydroxyalkyl radical), wherein R¹ and R² are the same or different and are selected from the group consisting of hydrogen, C₁ to C₄ alkyl or alkenyl and C₆ to C₉ aryl,

alkaryl or aralkyl and R^7 is hydrogen, C_1 to C_4 unsubstituted or substituted alkyl or alkenyl wherein the substituents are selected from those designated as Z above or C_6 to C_9 unsubstituted or substituted aryl, alkaryl or aralkyl wherein the substituents are selected from those defined as Z above and
 5 wherein X is as defined in formula (I).

Specific examples of formula (IV) compounds are:

aniline, p-chloroaniline, p-fluoroaniline, p-nitroaniline, p-aminobenzaldehyde, p-aminobenzoic acid, sodium-p-aminobenzoate, lithium-p-aminobenzoate, calcium di-p-aminobenzoate, ammonium-p-aminobenzoate,
 10 trimethylammonium-p-aminobenzoate, tri(2-hydroxyethyl)-p-aminobenzoate, p-aminobenzenesulfonic acid, potassium p-aminobenzenesulfonate, N-methylaniline, N-propyl-N-phenylaniline, N-methyl-N-2-propenylaniline, N-benzylaniline, N-(2-ethylphenyl)aniline, 4-methylaniline, 4-(2-bromoethyl)aniline, 2-(2-nitroethyl)aniline, (4-aminophenyl)acetaldehyde, (4-aminophenyl)acetic acid, 4-(2-propenyl)aniline acetate, 4-(3-bromo-2-propenyl)aniline, 4-phenylaniline chloroacetate, 4-(3-chlorophenyl)aniline, 4-benzylaniline, 4-(4-iodobenzyl)aniline, 4-(3-ethylphenyl)aniline, 4-(2-chloro-4-ethylphenyl)aniline.

20



25

wherein Z and R^7 are defined as in formula (IV) and R^8 is hydrogen or C_1 to C_4 substituted or unsubstituted alkyl or alkenyl wherein the substituents are selected from those defined as Z in formula (IV).

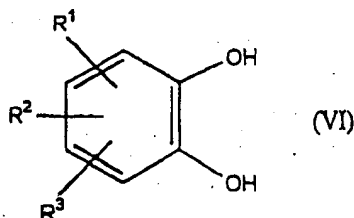
Specific examples of formula (V) compounds are:

phenol, p-chlorophenol, p-nitrophenol, p-hydroxybenzaldehyde, p-hydroxybenzoic acid, p-hydroxybenzenesulfonic acid, ethylphenyl ether, 2-chloroethylphenyl ether, 2-nitroethylphenyl ether, phenoxyacetaldehyde,
 30 phenoxyacetic acid, 3-phenoxy-1-propene, 3-phenoxy-2-nitro-1-propene, 3-phenoxy-2-bromo-1-propene, 4-propylphenol, 4-(3-bromopropyl)phenol, 2-

(2-nitroethyl)phenol, (4-hydroxyphenyl)acetaldehyde, (4-hydroxyphenyl)acetic acid, 4-(2-propenyl)phenol, 4-phenylphenol, 4-benzylphenol, 4-(3-fluoro-2-propenyl)phenol, 4-(4-chlorobenzyl)phenol, 4-(3-ethylphenyl)phenol, 4-(2-chloro-3-ethylphenyl)phenol, 2,5-xylenol, 2,5-diaminopyridine, 2-hydroxy-5-aminopyridine, 2-amino-3-hydroxy pyridine, tetraaminopyrimidine, 1,2,4-trihydroxybenzene, 1,2,4-trihydroxy-5-(C1-C6-alkyl)benzene, 1,2,3-trihydroxybenzene, 4-aminoresorcinol, 1,2-dihydroxybenzene, 2-amino-1,4-dihydroxybenzene, 2-amino-4-methoxyphenol, 2,4-diaminophenol, 3-methoxy-1,2-dihydroxybenzene, 1,4-dihydroxy-2-(N,N-diethylamino)benzene, 2,5-diamino-4-methoxy-1-hydroxybenzene, 4,6-dimethoxy-3-amino-1-hydroxybenzene, 2,6-dimethyl-4-[N-(p-hydroxyphenyl)amino]-1-hydroxybenzene, 1,5-diamino-2-methyl-4-[N-(p-hydroxyphenyl)amino]benzene and salts thereof.

Additional primary intermediates suitable for use herein include catechol species and in particular catechol "dopa" species which includes dopa itself as well as homologs, analogs and derivatives of DOPA. Examples of suitable catechol species include cysteinyl dopa, alpha alkyl dopa having 1 to 4, preferably 1 to 2 carbon atoms in the alkyl group, epinephrine and dopa alkyl esters having 1 to 6, preferably 1 to 2 carbon atoms in the alkyl group.

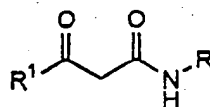
In general suitable catechols are represented by formula (VI) below:



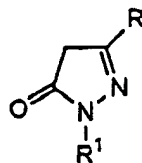
wherein R^1 , R^2 and R^3 , which may be the same or different, are electron donor or acceptor substituents selected from H, lower (C_1 - C_6) alkyl, OH, OR, COOR, NHCOR, CN, COOH, Halogen, NO_2 , CF_3 , SO_3H or NR^4R^5 , with the proviso that only one of the R^1 , R^2 or R^3 can be CN, COOH, halogen, NO_2 , CF_3 or SO_3H ; R^4 and R^5 , which may be the same or different, are H, lower (C_1 - C_6) alkyl or substituted lower (C_1 - C_6) alkyl in which the substituent

may be OH, OR, NHCOR⁶, NHCONH₂, NHCO₂R⁶, NHCSNH₂, CN, COOH, SO₃H, SO₂NR⁶, SO₂R⁶ or CO₂R⁶; R⁶ is lower (C₁-C₆) alkyl, lower (C₁-C₆) hydroxyalkyl phenyl linked to the nitrogen by an alkylene chain, phenyl or substituted phenyl with the substituent defined as R¹, and R is C₁-C₆ alkyl or C₁-C₆ hydroxyalkyl.

Also included herein are oxidative hair coloring agents of the formula:

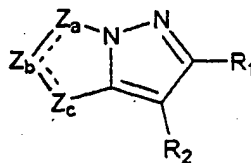


wherein: R¹ = substituted or unsubstituted benzene ring, tertiary-butyl, etc.;
R = substituted or unsubstituted benzene ring and the formula:



wherein R = aminoalkyl, amidoalkyl, aminobenzene (substituted or unsubstituted), amidobenzene (substituted or unsubstituted), alkyl, substituted or unsubstituted benzene ring; R¹ = substituted or unsubstituted benzene ring. These oxidative hair coloring agents are generally referred to as photographic dyes and include those disclosed in WO98/52519, WO98/52520, WO98/52521, WO98/52522, WO98/52523, and can be used in the present invention.

Pyrazoloazole type couplers may also be used in the color altering compositions of the present invention. Such compounds have the general structure below



wherein Z_a, Z_b, and Z_c are individually selected from carbon or nitrogen, which may optionally have substituents. R₁ and R₂ are individually selected

from the group consisting of H, alkyl, alkenyl, alkynyl, aryl, alkaryl, aralkyl, amine, alkyl substituted with one of more nitrogen or sulfur atom, alkenyl substituted with one of more nitrogen or sulfur atom, alkynyl substituted with one of more nitrogen or sulfur atom, aryl substituted with one of more
5 nitrogen or sulfur atom, alkaryl substituted with one of more nitrogen or sulfur atom, aralkyl substituted with one of more nitrogen or sulfur atom, and halogens.

Where Z_a , Z_b , and Z_c have substituents, they are preferably selected from the same groups as defined for R_1 and R_2 .

10 The primary intermediates can be used herein alone or in combination with other primary intermediates, and one or more can be used in combination with one or more couplers. The choice of primary intermediates and couplers will be determined by the color, shade and intensity of coloration which is desired. There are nineteen preferred primary
15 intermediates and couplers which can be used herein, singly or in combination, to provide dyes having a variety of shades ranging from ash blonde to black; these are: pyrogallol, resorcinol, p-toluenediamine, p-phenylenediamine, o-phenylenediamine, m-phenylenediamine, o-aminophenol, p-aminophenol, 4-amino-2-nitrophenol, nitro-p-
20 phenylenediamine, N-phenyl-p-phenylenediamine, m-aminophenol, 2-amino-3-hydroxypyridine, 1-naphthol, [N,N bis (2-hydroxyethyl)p-phenylenediamine], 4-amino-2-hydroxytoluene, 1,5-dihydroxynaphthalene, 2-methyl resorcinol and 2,4-diaminoanisole. These can be used in the molecular form or in the form of peroxide-compatible salts, as detailed above.

25 For example low intensity colors such as natural blond to light brown hair shades generally comprise from about 0.001% to about 5%, preferably from about 0.1% to about 2%, more preferably from about 0.2% to about 1% by weight of coloring composition of total oxidative dyeing agents and may be achieved by the combination of primary intermediates such as 1,4-
30 diamino-benzene, 2,5-diamino toluene, 2,5-diamino-anisole, 4-aminophenol, 2,5-diamino-benzyl alcohol and 2-(2',5'-diamino)phenyl-ethanol with couplers such as resorcinol, 2-methyl resorcinol or 4-chloro resorcinol.

Similarly combination of the above primary intermediates with couplers, such as, 5-amino-2-methyl phenol and 1,3-diamino-benzene derivatives such as 2,4-diamino-anisole at levels of from about 0.5% to about 1% of total dyeing agents can lead to medium intensity red colors.

5 High intensity colors such as blue to blue-violet hair shades can be produced by the combination of the above primary intermediates with couplers such as 1,3-diamino-benzene or its derivatives such as 2,5-diamino-toluene at levels of from about 1% to about 6% by weight of composition of total dyeing agents. Black hair colors can be obtained by
10 combining the aforementioned primary intermediates with couplers such as 1,3-diaminobenzene or its derivatives

Particularly preferred oxidative dyes utilised in the compositions used in the present invention include para-phenylene diamine, para-aminophenol, 2-amino-3-hydroxy pyridine, resorcinol, 4-amino-2-hydroxy
15 toluene, meta-phenylene diamine, meta-aminophenol [N,N bis (2-hydroxyethyl)p-phenylenediamine], α -naphthol, 2,5-diaminotoluene sulphate and ortho-aminophenol.

Non-oxidative and other dyes

The coloring altering compositions utilised in the present invention
20 may, in addition to an oxidative hair coloring agent, include non-oxidative and other dye materials. Optional non-oxidative and other dyes suitable for use in the hair coloring compositions and processes according to the present invention include both semi-permanent, temporary and other dyes. Non-oxidative dyes as defined herein include the so-called 'direct action dyes',
25 metallic dyes, metal chelate dyes, fibre reactive dyes and other synthetic and natural dyes. Various types of non-oxidative dyes are detailed in: 'Chemical and Physical Behaviour of Human Hair' 3rd Ed. by Clarence Robbins (pp250-259); 'The Chemistry and Manufacture of Cosmetics'. Volume IV. 2nd Ed. Maison G. De Navarre at chapter 45 by G.S. Kass (pp841-920);
30 'cosmetics: Science and Technology' 2nd Ed., Vol. II Balsam Sagarin, Chapter 23 by F.E. Wall (pp 279-343); 'The Science of Hair Care' edited by

C. Zviak, Chapter 7 (pp 235-261) and 'Hair Dyes', J.C. Johnson, Noyes Data Corp., Park Ridge, U.S.A. (1973), (pp 3-91 and 113-139).

Direct action dyes which do not require an oxidative effect in order to develop the color, are also designated hair tints and have long been known in the art. They are usually applied to the hair in a base matrix which includes surfactant material. Direct action dyes include nitro dyes such as the derivatives of nitroamino benzene or nitroaminophenol; disperse dyes such as nitroaryl amines, aminoanthraquinones or azo dyes; anthraquinone dyes, naphthoquinone dyes; basic dyes such as Acridine Orange C.I. 46005.

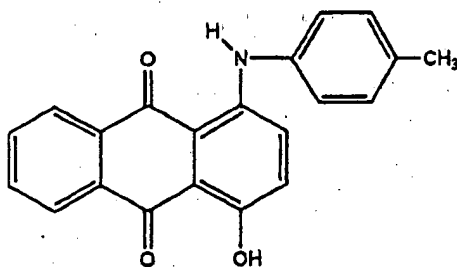
Nitrodyes are added to dyeing compositions to enhance color of colorant and to add suitable aesthetic color to the dye mixture prior to application.

Further examples of direct action dyes include the Arianor dyes basic brown 17, C.I.(color index) - no. 12,251; basic red 76, C.I. - 12,245; basic brown 16, C.I. - 12,250; basic yellow 57, C.I. - 12,719 and basic blue 99, C.I. - 56,059 and further direct action dyes such as acid yellow 1, C.I. - 10,316 (D&C yellow no.7); acid yellow 9, C.I. - 13,015; basic violet C.I. - 45,170; disperse yellow 3, C.I. - 11,855; basic yellow 57, C.I. - 12,719; disperse yellow 1, C.I. - 10,345; basic violet 1, C.I. - 42,535, basic violet 3, C.I. - 42,555; greenish blue, C.I. - 42090 (FD&C Blue no.1); yellowish red, C.I. - 14700 (FD&C red no.4); yellow, C.I.19140 (FD&C yellow no5); yellowish orange, C.I.15985 (FD&C yellow no.6); bluish green, C.I.42053 (FD&C green no.3); yellowish red, C.I.16035 (FD&C red no.40); bluish green, C.I.61570 (D&C green no.3); orange, C.I.45370 (D&C orange no.5); red, C.I.15850 (D&C red no.6); bluish red, C.I.15850(D&C red no.7); slight bluish red, C.I.45380(D&C red no.22); bluish red, C.I.45410(D&C red no.28); bluish red, C.I.73360(D&C red no.30); reddish purple, C.I.17200(D&C red no.33); dirty blue red, C.I.15880(D&C red no.34); bright yellow red, C.I.12085(D&C red no.36); bright orange, C.I.15510(D&C orange no.4); greenish yellow, C.I.47005(D&C yellow no.10); bluish green, C.I.59040(D&C green no.8); bluish violet, C.I.60730(Ext. D&C violet no.2); greenish yellow, C.I.10316(Ext. D&C yellow no.7);

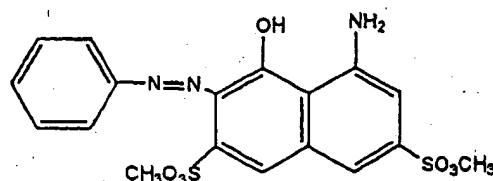
Fibre reactive dyes include the Procion (RTM), Drimarene (RTM), Cibacron (RTM), Levafix (RTM) and Remazol (RTM) dyes available from ICI, Sandoz, Ciba-Geigy, Bayer and Hoechst respectively.

Natural dyes and vegetable dyes as defined herein include henna
5 (*Lawsonia alba*), camomile (*Matricaria chamomila* or *Anthemis nobilis*), indigo, logwood and walnut hull extract.

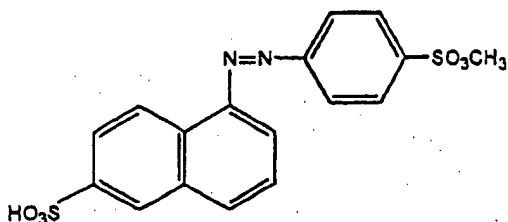
Temporary hair dyes, or hair coloring rinses, are generally comprised of dye molecules which are too large to diffuse into the hair shaft and which act on the exterior of the hair. They are usually applied via a leave-in
10 procedure in which the dye solution is allowed to dry on the hair surface. As such these dyes are typically less resistant to the effects of washing and cleaning the hair with surface active agents and are washed off of the hair with relative ease. Any temporary hair dye may suitably be used in the compositions of the invention and examples of preferred temporary hair dyes
15 are illustrated below.



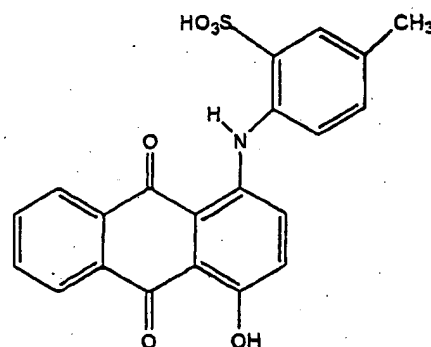
Violet



Red

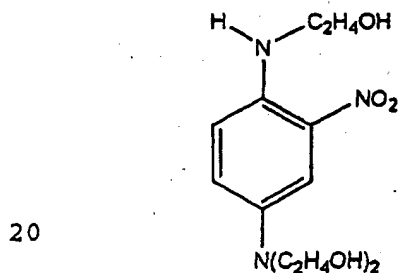


Yellow

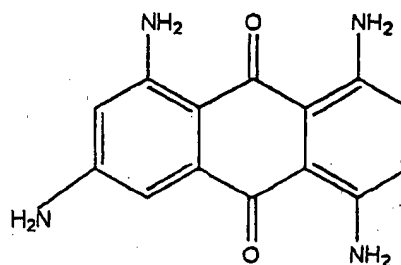


Blue-Violet

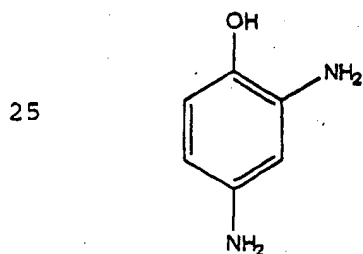
Semi-permanent hair dyes are dyes which are generally smaller in size and effect to temporary hair rinses but are generally larger than permanent (oxidative) dyes. Typically, semi-permanent dyes act in a similar manner to oxidative dyes in that they have the potential to diffuse into the hair shaft. However, semi-permanent dyes are generally smaller in size than the aforementioned conjugated oxidative dye molecules and as such are pre-disposed to gradual diffusion out of the hair again. Simple hair washing and cleaning action will encourage this process and in general semi-permanent dyes are largely washed out of the hair after about 5 to 8 washes. Any semi-permanent dye system may be suitably used in the compositions of the present invention. Suitable semi-permanent dyes for use in the compositions of the present invention are HC Blue 2, HC Yellow 4, HC Red 3, Disperse Violet 4, Disperse Black 9, HC Blue 7, HC Yellow 2, Disperse Blue 3, Disperse violet 1 and mixtures thereof. Examples of semi-permanent dyes are illustrated below:



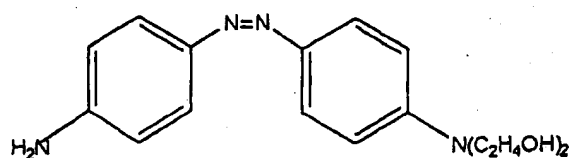
Blue



Blue



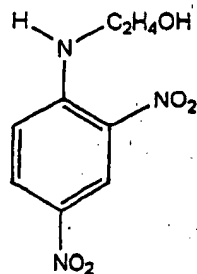
Yellow



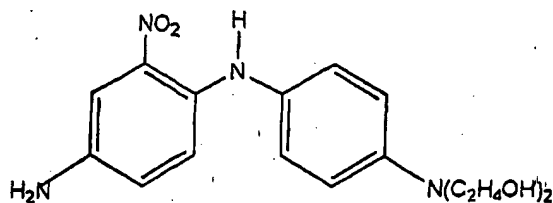
Yellow

42

5



Red



Red

Typical semi-permanent dye systems incorporate mixtures of both large and small color molecules. As the size of the hair is not uniform from root to tip the small molecules will diffuse both at the root and tip, but will not be retained within the tip, while the larger molecules will be generally only be able to diffuse into the ends of the hair. This combination of dye molecule size is used to help give consistent color results from the root to the tip of the hair both during the initial dyeing process and during subsequent washing.

Catalyst

The color altering compositions used herein may optionally contain a transition metal containing catalyst for the inorganic peroxygen oxidising agents and the, optional, preformed peroxy acid oxidising agent(s). One suitable type of catalyst is a catalyst system comprising a heavy metal cation of defined bleach catalytic activity, such as copper, iron or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminium cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra (methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in US-A-4,430,243.

Other types of suitable catalysts include the manganese-based complexes disclosed in US-A-5,246,621 and US-A-5,244,594. Preferred examples of these catalysts include $\text{MnIV}_2(\mu\text{-O})_3(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{PF}_6)_2$, $\text{MnIII}_2(\mu\text{-O})_1(\mu\text{-OAc})_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{MnIV}_4(\mu\text{-O})_6(1,4,7\text{-triazacyclononane})_4$

(ClO₄)₂, MnIII MnIV₄(μ-O)1(μ-OAc)2-(1,4,7-trimethyl-1,4,7-triazacyclononane)2-(ClO₄)₃, and mixtures thereof. Others are described in EP-A-0,549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

For examples of suitable catalysts see US-A-4,246,612 and US-A-5,227,084. See also US-A-5,194,416 which teaches mononuclear manganese (IV) complexes such as Mn(1,4,7-trimethyl-1,4,7-triazacyclononane)(OCH₃)₃-(PF₆). Still another type of suitably catalyst, as disclosed in US-A-5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Other examples include binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including N₄MnIII(μ-O)₂MnIVN₄ and [Bipy₂MnIII(μ-O)₂MnIVbipy₂](ClO₄)₃.

Further suitable catalysts are described, for example, in EP-A-0,408,131 (cobalt complex catalysts), EP-A-0,384,503, and EP-A-0,306,089 (metallo-porphyrin catalysts), US-A-4,728,455 (manganese/multidentate ligand catalyst), US-A-4,711,748 and EP-A-0,224,952, (absorbed manganese on aluminosilicate catalyst), US-A-4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), US-A-4,626,373 (manganese/ligand catalyst), US-A-4,119,557 (ferric complex catalyst), DE-A-2,054,019 (cobalt chelant catalyst) CA-A-866,191 (transition metal-containing salts), US-A-4,430,243 (chelants with manganese cations and non-catalytic metal cations), and US-A-4,728,455 (manganese gluconate catalysts).

Heavy metal ion sequestrant

The color altering compositions utilised in the invention may contain as an optional component a heavy metal ion sequestrant. Heavy metal ion sequestrants are components which act to sequester (chelate or scavenge) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to

binding heavy metal ions such as iron, manganese and copper. Such sequestering agents are valuable in hair coloring compositions as herein described for the delivery of controlled oxidising action as well as for the provision of good storage stability of the hair coloring products.

5 Heavy metal ion sequestrants are generally present at a level of from about 0.005% to about 20%, preferably from about 0.01% to about 10%, more preferably from about 0.05% to about 2% by weight of the compositions.

Various sequestering agents, including the amino phosphonates, available as Dequest (RTM) from Monsanto, the nitriloacetates, the hydroxyethyl-ethylene triamines and the like are known for such use. Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates.

15 Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene-1,1-diphosphonate.

20 Preferred biodegradable non-phosphorous heavy metal ion sequestrants suitable for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminetetracetic acid, ethylenetriamine pentaacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutaric acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof. Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS). see US-A-4,704,233, or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof.

Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in

EP-A-516,102 are also suitable herein. The -alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

5 EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequesterant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-N,N'-disuccinic acid (GADS),
10 ethylenediamine-N,N'-diglutamic acid (EDDG) and 2-hydroxypropylenediamine-N,N'-disuccinic acid (HPDDS) are also suitable.

The heavy metal ion sequestering agents utilised in the present invention may be used in their alkali or alkaline earth metal salts.

Particularly preferred combinations of heavy metal ion sequestering
15 agents for use herein include (a) sodium stannate, etidronic acid, and pentasodium pentatate, (b) sodium stannate, disodium pyrophosphate, sodium pentatate, © sodium stannate, disodium pyrophosphate and EDTA, (d) sodium stannate, etidronic acid and EDTA and (e) sodium stannate, disodium pyrophosphate and etidronic acid.

20 Peroxide stabilising agents

The color altering compositions of the present invention may additionally comprise an alkoxylated benzoic acid or a salt thereof which acts as a peroxide stabilising agent

Preferably, said alkoxylated benzoic acid or a salt thereof is selected
25 from the group consisting of a monoalkoxy benzoic acid, or a salt thereof, a dialkoxy benzoic acid, or a salt thereof, a trialkoxy benzoic acid, or a salt thereof; and mixtures thereof.

More preferably, the alkoxylated benzoic acid or the salt thereof is a trimethoxy benzoic acid or a salt thereof (TMBA).

30 Most preferably the alkoxylated benzoic acid or the salt thereof is selected from the group consisting of 3,4,5,- trimethoxy benzoic acid, a salt

thereof, 2,3,4- trimethoxy benzoic acid, a salt thereof, 2,4,5- trimethoxy benzoic acid, a salt thereof and mixtures thereof.

In an especially preferred embodiment, said alkoxyated benzoic acid is 3,4,5,- trimethoxy benzoic acid.

5 Suitable monoalkoxy benzoic acids or salts thereof are commercially available from Aldrich, in particular m-methoxy benzoic acid is commercially available from Aldrich. Suitable trimethoxy benzoic acids or salts thereof are commercially available from Aldrich and Merck.

Typically, the color altering composition utilised in the present
10 invention comprises from 0.001% to 5%, preferably from 0.005% to 2.5% and more preferably from 0.01% to 1.0% by weight of the total composition of said alkoxyated benzoic acid or a salt thereof.

It has now been found that an alkoxyated benzoic acid or a salt thereof, acts as a radical scavenger in the color altering composition of the
15 present invention. Indeed, the presence of an alkoxyated benzoic acid or a salt thereof, the color altering compositions significantly increases the immediate chemical stability and particularly the chemical stability upon storage of the peroxygen bleaching agents comprised in the color altering compositions utilised in the present invention.

20 Thickeners

The color altering compositions utilised in the present invention may additionally include a thickener at a level of from about 0.05% to about 20%, preferably from about 0.1% to about 10%, more preferably from about 0.5% to about 5% by weight. Thickening agents suitable for use in the
25 compositions herein are selected from oleic acid, cetyl alcohol, oleyl alcohol, sodium chloride, cetearyl alcohol, stearyl alcohol, synthetic thickeners such as Carbopol, Aculyn and Acrosyl and mixtures thereof. Preferred thickeners for use herein are Aculyn 22 (RTM), steareth-20 methacrylate copolymer; Aculyn 44 (RTM), polyurethane resin and Acusol 830 (RTM), acrylates
30 copolymer which are available from Rohm and Haas, Philadelphia, PA, USA. Additional thickening agents suitable for use herein include sodium alginate

or gum arabic, or cellulose derivatives, such as methyl cellulose or the sodium salt of carboxymethylcellulose or acrylic polymers.

Diluent

Water is the preferred diluent for the color altering compositions
5 utilised in the present invention. However, the compositions according to the present invention may include one or more solvents as additional diluent materials. Generally, solvents suitable for use in the coloring compositions are selected to be miscible with water and innocuous to the skin. Solvents
10 suitable for use as additional diluents herein include C₁-C₂₀ mono- or polyhydric alcohols and their ethers, glycerine, with monohydric and dihydric alcohols and their ethers preferred. In these compounds, alcoholic residues containing 2 to 10 carbon atoms are preferred. Thus, a preferred group
15 includes ethanol, isopropanol, n-propanol, butanol, propylene glycol, ethylene glycol monoethyl ether, and mixtures thereof. Water is the preferred principal diluent in the compositions according to the present
invention. Principal diluent, as defined herein, means, that the level of water present is higher than the total level of any other diluents.

The diluent is present at a level preferably of from about 5% to about 99.98%, preferably from about 15% to about 99.5%, more preferably at least
20 from about 30% to about 99%, and especially from about 50% to about 98% by weight of the compositions herein.

Enzyme

A further additional material useful in the color altering compositions according to the present invention is one or more enzymes.

25 Suitable enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, esterases, cellulases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

30 Peroxidases are haemoproteins specific for peroxide, but using a wide range of substances as donors. Catalase which decomposes peroxide, is included here in view of the fact that it is generally similar in structure and

properties and is able to bring about certain oxidations by H_2O_2 . The decomposition of H_2O_2 can be regarded as the oxidation of one molecule by the other. It is widespread in aerobic cells and may have some more important function. The coenzyme peroxidases are not haemoproteins and one at least is a flavoprotein. Other flavoproteins such as xanthine oxidase will also use H_2O_2 among other acceptors, and the coenzyme peroxidases resemble these rather than the classical peroxidases in not being specific for H_2O_2 . Suitable peroxidases for the compositions of the present invention include horseradish peroxidase, Japanese radish peroxidase, cow's milk peroxidase, rat liver peroxidase, liginase and haloperoxidase such as chloro- and bromo-peroxidase.

Enzymes are optionally incorporated at levels sufficient to provide up to about 50 mg by weight, more typically about 0.01mg to about 10 mg of active enzyme per gramm of the hair treatment composition of the invention. Stated otherwise the peroxidase enzyme may be incorporated into the compositions in accordance with the invention at a level of from about 0.0001% to about 5%, preferably from about 0.001% to about 1%, more preferably from about 0.01% to about 1% active enzyme by weight of the composition.

Commercially available protease enzymes include those sold under the trade names Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

Amylases include amylases obtained from a special strain of *B licheniformis*, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl and BAN by Novo Industries A/S. Amylase enzyme may be

incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Lipolytic enzyme may be present at levels of active lipolytic enzyme of from 0.0001% to 2% by weight, preferably 0.001% to 1% by weight, most
5 preferably from 0.001% to 0.5% by weight of the compositions.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of Humicola sp., Thermomyces sp. or Pseudomonas sp. including Pseudomonas pseudoalcaligenes or
10 Pseudomonas fluorescens. Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host,
15 as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Høge-Jensen et al, issued March 7, 1989.

Surfactant Materials

20 The color altering compositions utilised herein can additionally contain a surfactant system which may be any of those discussed above as being suitable for the pretreatment composition.

Optional Materials

A number of additional optional materials can be added to the color
25 altering compositions herein described. These may be selected from the same materials as defined as optional materials for use in the pretreatment compositions.

Experimental Methods

Assessment of Initial Color and Color Change

30 The equipment used to measure both the initial color and color change on substrates (hair / skin) dyed with the low pH coloring compositions of the present invention is a Hunter Colorquest spectrophotometer. The value used

to express the degree of color change on any particular substrate is ΔE . ΔE , as defined herein, is represented by a factual sum of L, a, and b values such that:

5
$$\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$$

and L is a measure of lightness and darkness (color intensity), wherein L = 100 is equivalent to white, and L = 0 is equivalent to black. Further, 'a' is a measure of the red and green quotients (color hues) such that positive equates to red and negative equates to green, and 'b' is a measure of the yellow and blue quotients (color hues) such that positive equates to yellow and negative equates to blue.

10 Spectrophotometric measurements can be carried out on the Hunter Labscan Colorimeter which is full scanning spectrophotometer with a wavelength of from 400-700 nanometers which records the color of test hair switches (tresses) in terms of 'L', 'a' and 'b' values. The machine is set to: mode - 0/45; port size - 1 inch; view size - 1 inch; light - D65; field of view - 10°; UV lamp/filter - none. The hair is placed in a sample holder designed to hold the hair in a uniform orientation during measurement. Equivalent colorimeters can be used, but it must be ensured that the hair does not move during measurement. The hair must be spread to cover the 1 inch port during color measurement. Dots are placed on the switch holder to guide the positioning of the holder at the port. The dots are lined up with a mark on the port and readings are taken at each spot.

25 8 measurements are run per switch, 4 on each side, and 1 switch is run per treatment.

Standard Hair Switch

The compositions according to the present invention can be used to color hair of all colors, types and condition. For the purposes of illustration a number of test hair switch types have been tested herein. These standard hair switches can be measured in terms of their approximate L, a, b values.

51

| | <u>L</u> | <u>a</u> | <u>b</u> |
|----------------------|----------|----------|----------|
| Virgin Yak | 82 | -1 | 12 |
| 5 Virgin light brown | 32 | 5 | 14 |

Hair Switch Coloring Method

To color hair, a 4 gramme switch of about 8 inch long hair is hung over a suitable container. The pretreatment composition is then applied to the hair, massaged into the hair and left in place for 5 minutes (1.5 grammes of pretreatment composition per gramme of hair). The test coloring product is then prepared (i.e., where applicable the separate bottle components are mixed together) and about 2 grammes of product is applied directly to the test hair switch without removal of the pretreatment composition. The colorant is massaged through the hair switch for up to about 1 minute and then left on the hair switch for up to about 30 minutes. After rinsing with running water for about 1 or 2 minutes the colored hair switch is then cleansed and dried. Drying can be effected either naturally (without heat assistance) or using a drier. The color development (initial color) of the colored, cleansed, dried test hair switch can then be assessed using the Hunter Colorquest spectrophotometer.

ExamplesAmmonium Carbonate Pretreatment Compositions

Formulation 1:

| | | |
|----|---------------------|-------|
| | Raw Material | % |
| 5 | Demineralised Water | 95.85 |
| | C-9-11 Pareth-8 | 0.25 |
| | Perfume | 0.5 |
| | Ammonium Carbonate | 2 |
| | Tetra Sodium EDTA | 0.1 |
| 10 | Phenoxyethanol | 0.3 |
| | Polyquaternium-4 | 0.5 |
| | PEG-40 | 0.5 |

Formulation 2:

| | | |
|----|---------------------|-------|
| 15 | Raw Material | % |
| | Demineralised Water | 93.25 |
| | C-9-11 Pareth-8 | 0.25 |
| | Perfume | 0.1 |
| | Ammonium Carbonate | 5 |
| 20 | Polyquaternium-4 | 0.5 |
| | Tetra Sodium EDTA | 0.1 |
| | phenoxyethanol | 0.3 |
| | PEG-40 | 0.5 |

25 The pH of the pretreatment formulations 1 and 2 is in the range 8.8 to 9.1.

Color UptakeColor altering Formulations

| | I | II | III | IV | V |
|------------------|---------|---------|---------|---------|---------|
| 5 Cetyl alcohol | 2.25 | 2.25 | 2.25 | 2.25 | 2.25 |
| Steareth alcohol | 2.25 | 2.25 | 2.25 | 2.25 | 2.25 |
| Ceteareth-25 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| PPD.2HCl | 0.4 | 0.17 | 0.1 | 1.0 | / |
| PAP | 0.3 | 0.17 | 0.75 | / | / |
| 10 AHP | 0.3 | / | 0.3 | / | / |
| 1-Naphthol | / | / | / | / | / |
| Resorcinol | / | / | / | 0.25 | / |
| AHT | / | / | / | / | 0.1 |
| MPD | / | / | / | 0.2 | / |
| 15 MAP | / | / | / | / | / |
| OAP | / | 0.17 | / | / | 0.1 |
| Sodium sulphite | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Ascorbic acid | 0.3 | / | 0.3 | 0.8 | / |
| EDTA | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 |
| 20 Citric acid | 0.5 | 0.8 | 0.8 | 0.8 | 0.8 |
| H ydrogen | 3 | 3 | 3 | 3 | 3 |
| Peroxide | | | | | |
| Sodium hydroxide | to pH 5 | to pH 5 | to pH 5 | to pH 5 | to pH 5 |
| 25 Water | qs 100 | 100 | 100 | qs 100 | 100 |

PAP = para-aminophenol

AHP = 2-amino-3-hydroxypyridine

PPD.2HCl = paraphenylene diamine. 2HCl

AHT = 4-amino-2-hydroxytoluene

30 MPD = meta-phenylene diamine

MAP = meta-aminophenol

OAP = ortho-aminophenol..

Color Results

35 Pretreatment Formulation 1 is applied to untreated Yak switch for 5 minutes followed by color altering formulation for 30mins at 30°C.

| | | | | |
|----|-------------|--------------|------------|--------------------|
| | Formulation | Pretreatment | ΔE | Visual color |
| | I | No | 50 | Light Orange/Brown |
| | I | Yes | 58 | Light Red/brown |
| 5 | II | No | 51 | Light Brown |
| | II | Yes | 57 | Light Brown |
| | III | No | 60 | Red/Brown |
| | III | Yes | 69 | Dark Auburn |
| | IV | No | 68 | Dark Grey |
| 10 | IV | Yes | 72 | Black |
| | V | No | 1.8 | Light Brown |
| | V | Yes | 6.6 | Mid Blonde |

The results show that a greater colour change (ΔE) is achieved utilising the pretreatment composition compared to no pretreatment.

Damage

Pretreatment formulation 1 was applied to the hair for 5 minutes then dye formulation III was applied to the hair for 30mins at 30°C. On drying, the cysteic acid content was measured using FTIR (Fourier Transform Infra Red) and the ΔE measured using UV/vis as discussed above. The process was repeated for 2, 3 and 4 cycles. A second set of results were generated without the pretreatment.

Results

| | | | | |
|----|-------------------------------|---------------------------|------------------|-----------------------|
| | Number of Pretreatment Cycles | Number of Colorant Cycles | ΔE color | Relative Cysteic Acid |
| 25 | 0 | 1 | 50.7 | 1.0 |
| | 0 | 2 | 56.9 | |
| | 0 | 3 | 60.2 | |
| | 0 | 4 | 62.9 | |
| 30 | 1 | 1 | 59.0 | 1.03 |
| | 2 | 2 | 64.1 | |
| | 3 | 3 | 66.6 | |
| | 4 | 4 | 68.0 | |

The results show that a similar amount of damage is inflicted on the hair whilst providing a large increase in the ΔE colour uptake.

Pretreatment formulation 2 was applied to the hair for 5 minutes then Dye formulation V applied for 30mins at 30°C. On drying the cysteic acid and ΔE were measured.

| Number of Pretreatment Cycles | Number of Colorant Cycles | ΔE | Relative Cysteic Acid |
|-------------------------------|---------------------------|------------|-----------------------|
| 0 | 1 | 3.7 | 1.0 |
| 0 | 2 | 4.3 | |
| 0 | 3 | 6.3 | |
| 0 | 4 | 7.3 | |
| 1 | 1 | 6.5 | 1.11 |
| 2 | 2 | 7.7 | |
| 3 | 3 | 9.8 | |
| 4 | 4 | 11.0 | |

Fade

Switches were dyed with formulations I, II and IV with and without 2% ammonium carbonate pretreatment (Pretreatment formulation 1). Switches were then put through 40 shampoo washing cycles and the loss of color measured.

| Formulation | Pretreatment | Substrate | ΔE fade (40wash) | % Fade |
|-------------|--------------|--------------------|--------------------------|--------|
| I | No | Virgin Yak | 3.6 | 6.5 |
| I | Yes | Virgin Yak | 2.8 | 4.4 |
| I | No | Virgin Light Brown | 1.8 | 12.1 |
| I | Yes | Virgin Light Brown | 1.0 | 5.4 |
| II | No | Virgin Yak | 2.2 | 4.7 |
| II | Yes | Virgin Yak | 1.0 | 1.8 |
| II | No | Virgin Light Brown | 1.8 | 21.6 |
| II | Yes | Virgin Light Brown | 0.8 | 8.8 |
| IV | No | Virgin Yak | 5.8 | 8.5 |
| IV | Yes | Virgin Yak | 2.6 | 3.6 |
| IV | No | Virgin Light Brown | 3.5 | 16.7 |
| IV | Yes | Virgin Light Brown | 1.2 | 5.8 |

The results show that for pretreated hair, the ΔE fade is considerably less than that for non-pretreated hair.

Claims:

1. A method of altering hair color comprising the steps of
 - (a) applying a pretreatment composition, which has a pH in the range 1 to 13, to the hair to be colored, the pretreatment composition being substantially free of hair color altering agents; and
 - (b) applying to the hair, in a subsequent step, a color altering composition which has a pH in the range 1 to 13, and the pH of the pretreatment composition is higher than the pH of the color altering composition; wherein the pretreatment composition is not rinsed from the hair prior to the application of the color altering composition.
2. A method according to claim 1, wherein the pretreatment composition has a pH in the range of 7.5 to 12 and the color altering composition has a pH in the range 1 to 7.
3. A method according to claim 1 or 2, wherein the pretreatment composition comprises an alkalisising agent selected from the group consisting of sodium hydroxide, ammonia, potassium hydroxide, piperidine, an alkylamine, such as mono-, di- or tri-methylamine, mono-, di- or tri-ethylamine, mono-, di- or tri-propylamine, mono-, di- or tri-butylamine, mono-, di- or tri-isopropylamine, isobutylamine, tert.-butylamine, an amylamine, myristylamine or laurylamine, ethylenediamine, an alkanolamine, such as mono-, di- or tri-ethanolamine, mono-, di- or tri-propanolamine, mono-, di- or tri-isopropanolamine or 2-amino-2-methylpropanol, 2-amino-2-methylpropane-1,3-diol, an alkylalkanolamine; sodium carbonate, potassium carbonate, ammonium carbonate, sodium hydrogen carbonate, potassium hydrogen carbonate, ammonium hydrogen carbonate, sodium carbamate, potassium carbamate, ammonium carbamate, and mixtures thereof.
4. A method according to claim 2, wherein the alkalisising agent is capable of generating HCO_3^- ions in solution.
5. A method according to claim 3 or claim 4, wherein the alkalisising agent is ammonium carbonate, ammonium hydrogen carbonate or a mixture thereof, preferably ammonium carbonate.

6. A method according to any of claims 3 to 5, wherein the alkalisising agent is present in a concentration of from 0.1% to 5%, preferably from 1.5% to 5.5% by weight.
7. A method according to any preceding claim wherein the pretreatment
5 composition has a pH in the range of 6 to 13, more preferably 7.5 to 12, more preferably 8 to 10, most preferably 8.5 to 9.5 and especially 8.7 to 9.2.
8. A method according to any preceding claim wherein the color altering composition comprises an oxidising agent, preferably an inorganic oxidising agent, more preferably hydrogen peroxide.
- 10 9. A method according to claim 8 wherein the oxidising agent is present at a level of from 0.01% to 10%, preferably from 0.01% to 6%, most preferably from 1% to 4.5% by weight of the color altering composition.
10. A method according to any preceding claim, wherein the color altering composition comprises at least one oxidative coloring agent.
- 15 11. A method according to any preceding claim wherein the hair color altering composition has pH in the range of 1 to 9, preferably 1.5 to 7, more preferably 2 to 6, in particular 2.5 to 5.8 and especially 3.5 to 5.5.
12. A method according to any preceding claim, wherein the pretreatment composition is applied directly to the hair and left in place for between 30
20 seconds and 20 minutes, prior to the application of the color altering composition, preferably 1 to 10 minutes, more preferably 2 to 6 minutes, most preferably 3 to 5 minutes.
13. Use of a pretreatment composition which has a pH in the range 6 to 13 for increasing the ability to alter hair color (ΔE uptake), of a color altering
25 composition containing at least one oxidative coloring agent.
14. Use of a pretreatment composition which has a pH in the range 6 to 13 for increasing fade resistance (ΔE fade) of colored hair, wherein the hair is treated with a color altering composition containing at least one oxidative coloring agent subsequent to application of the pretreatment composition.
- 30 15. Use of a pretreatment according to claim 13 or claim 14, wherein the pH of the oxidative coloring composition is in the range of 1 to 9, preferably 1.5 to 7, more preferably 2 to 6, in particular 2.5 to 5.8 and especially 3.5 to 5.5.

16. A kit comprising a pretreatment composition as defined in any of claims 1 to 5, and a hair color altering composition as defined in claims 1 and 6 to 9.
17. A kit according to claim 16, additionally comprising instructions for use of the pretreatment and hair color altering composition, wherein the instructions
5 include instructions for use as defined in claim 12.
18. A method of altering hair color comprising the steps of
- (a) applying a pretreatment composition comprising ammonium carbonate and/or ammonium hydrogen carbonate, which has a pH in the range 1 to 13, to the hair to be colored, the pretreatment
10 composition being substantially free of hair coloring agents; and
- (b) applying to the hair in a subsequent step, a color altering composition.
19. A method according to claim 18, wherein the color altering composition comprises an oxidising agent, preferably an inorganic oxidising agent, more
15 preferably hydrogen peroxide.
20. A method according to claim 19 wherein the oxidising agent is present at a level of from 0.01% to 10%, preferably from 0.01% to 6%, most preferably from 1% to 4.5% by weight of the color altering composition.
21. A method according to any of claims 18 to 20, wherein the color altering
20 composition comprises at least one oxidative coloring agent.
22. A method according to any of claims 18 to 21, wherein the pretreatment composition has pH in the range of 6 to 13, more preferably 7.5 to 12, more preferably 8 to 10, most preferably 8.5 to 9.5 and especially 8.7 to 9.2.
23. A method according to any of claims 18 to 22, wherein the hair color
25 altering composition has pH in the range of 1 to 9, preferably 1.5 to 7, more preferably 2 to 6, in particular 2.5 to 5.8 and especially 3.5 to 5.5.
24. A method according to any of claims 18 to 23, wherein the pretreatment composition remains on the hair when the color altering composition is applied.
25. A method according to any of claims 18 to 24, wherein the pretreatment
30 composition is applied directly to the hair and left in place for between 30 seconds and 20 minutes, prior to the application of the color altering

composition, preferably 1 to 10 minutes, more preferably 2 to 6 minutes, most preferably 3 to 5 minutes.

26. A method of altering hair color comprising the steps of

(a) applying a pretreatment composition, which has a pH in the range
5 1 to 13, to the hair to be colored, the pretreatment composition
being substantially free of hair color altering agents; and

(b) applying to the hair, in a subsequent step, a color altering
composition which has a pH in the range 1 to 6, and the pH of the
pretreatment composition is higher than the pH of the color
10 altering composition.

27. A method according to claim 26, wherein the color altering composition
has a pH in the range 2 to 6, preferably 2.5 to 5.8 most preferably 3.5 to 5.5.

28. A method according to claim 26 or 27, wherein the pretreatment
composition comprises any of the features of claims 2 to 7.

15 29. A method according to claim 26, 27 or 28, wherein the color altering
composition comprises any of the features of claims 8 to 10.

INTERNATIONAL SEARCH REPORT

national Application No
PCT/US 01/05598A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61K7/13

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X | DATABASE CHEMICAL ABSTRACTS 'Online! STN; ACCESS NUMBER 90: 92 263, XP002171264 abstract & JP 53 130443 A (SHISEIDO CO., LTD) 14 November 1978 (1978-11-14) | 1 |
| X | DATABASE CHEMICAL ABSTRACTS 'Online! STN; access number 131: 23 219, XP002171265 abstract & JP 11 139940 A (SEIWA KASEI K.K.) 25 May 1999 (1999-05-25) -/- | 1 |

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

5 July 2001

Date of mailing of the international search report

17/07/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Glikman, J-F

INTERNATIONAL SEARCH REPORT

national Application No

PCT/US 01/05598

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|---|-----------------------|
| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| X,P | DATABASE CHEMICAL ABSTRACTS 'Online! STN; access number 133:182 711, XP002171266 abstract & JP 2000 229821 A (NAKANO SEIYAKU K.K.) 22 August 2000 (2000-08-22) ----- | 1 |
| A | DATABASE CHEMICAL ABSTRACTS 'Online! STN; access number 117: 97 103, XP002171267 abstract & JP 04 069324 A (YAMAHATSU SANGYO K.K.) 4 March 1992 (1992-03-04) ----- | 1 |
| A | US 4 971 596 A (J. GROLLIER) 20 November 1990 (1990-11-20) claim 1 ----- | 1 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/05598

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|--|--|
| JP 53130443 A | 14-11-1978 | JP 1214495 C JP 58045401 B | 27-06-1984 08-10-1983 |
| JP 11139940 A | 25-05-1999 | NONE | |
| JP 2000229821 A | 22-08-2000 | NONE | |
| JP 04069324 A | 04-03-1992 | JP 2876247 B | 31-03-1999 |
| US 4971596 A | 20-11-1990 | LU 86521 A BE 1001000 A CA 1293452 A CH 672594 A DE 3723749 A FR 2601587 A GB 2192645 A,B IT 1211342 B JP 63033320 A | 02-02-1988 06-06-1989 24-12-1991 15-12-1989 21-01-1988 22-01-1988 20-01-1988 18-10-1989 13-02-1988 |

THIS PAGE BLANK (USPTO)